2017

Scaling understanding of biochar aging impacts on soil water and crop yields

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Scaling understanding of biochar aging impacts on soil water and crop yields

by

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A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Co-Majors: Soil Science (Soil Chemistry) and Environmental Science

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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2017

DEDICATION

To my family, without your constant love and support I would not be where I am today.

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ACKNOWLEDGMENTS

This dissertation was made possible through the support and input of many people and funding from multiple sources.

I would like to thank my major professor, David Laird, for giving me the opportunity to conduct this research, for challenging me, and always striving to make me a better scientist, writer, and communicator. Many thanks to my committee members, Rick Cruse, Sotirios Archontoulis, Robert Horton, and Jerry Hatfield, for their guidance, insight, and continuous encouragement throughout the course of my PhD. Also, thank you to my colleagues, the faculty, and staff in the Department of Agronomy for providing me with the resources and support I needed to advance in my degree and for making my time at ISU a great experience. Special thanks to members of my lab, in particular, Samuel Rathke, Rivka Fidel, Santanu Bakshi, and Chumki Banki for their assistance with and input in various aspects of my research.

To the many friends I have made in Iowa- Thank you! It is impossible to mention all those who have contributed to my success and have been a part of my ‘Iowa experience’, but some people include: Marie Bourguignon, Samantha Jones, Laila Puntel, Carolina Bermudez, Hanna Poffenbarger, Katie Taylor, Hamze Dookohaki, Marianne Emery, Melissa Spadaro, Gonza Parra, Daniel Kohlhase, Catherine Delong, and Carolina Cordova. More than just a thank you goes to Mauricio Tejera. Mauri, you have been my other half in this journey; celebrating with me during times of success and encouraging me to keep going during times of failure.

Lastly, I want to thank my parents, Bob and Josie Aller. Mom and Dad, there are no words that describe how much you have helped and supported me along the way. You both instilled in me a love for science and discovery from a very young age. I never thought as a child that getting to travel with you on fieldwork to Australia, Iceland, Costa Rica, etc., would have such a lasting impact on me, but it did and I thank you so much for those experiences.

Funding for this research was provided by the Global Climate and Energy Project, Stanford Subaward Agreement No. 60413992-112883-A, the National Science Foundation under Grant Number EPS-1101284, and the USDA-NIFA Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30411. Further support was provided by the Vernon C. Miller Endowed Scholarship and Oblinger Graduate Travel Funds.

ABSTRACT

Finding solutions to food-water-energy nexus challenges requires a systems approach and integration across scales to address issues of food production, environmental degradation, and energy use. Biochar, the co-product of thermochemical conversion of biomass to bioenergy, is a soil amendment that has the potential to improve soil quality, water retention, and crop productivity, while sequestering atmospheric C. Most of the positive benefits of biochar applications are based on evidence from short-term studies using freshly produced biochars, however, the effect of fresh and aged biochars over longer time periods remains inconclusive. This dissertation presents a series of integrated studies across the laboratory, greenhouse, field, and modeling scales to advance understanding of the impacts of biochar type and biochar aging on soil physical and chemical properties, soil water dynamics, and crop productivity. In the first study (Chapter 2), we developed a modified proximate analysis method that accounted for biochar diversity and found that volatile matter/fixed carbon ratios were a useful measure of biochar C stability. Using soil cores collected from a long-term bioenergy cropping system experiment we showed that crop rotations increased soil C and N, soil C/N ratio, pH and gravity drained water content, and decreased bulk density for soils with biochar relative to no-biochar controls (Chapter 3). A greenhouse soil column study (Chapter 4) showed that aged biochars impacted soil water relations differently than the equivalent fresh biochars. Biochar applications must be made strategically and take into account biochar type, soil type, and biochar age. The final two studies utilized the biochar model within the APSIM cropping systems model. In Chapter 5, we provided experimental verification of the pedotransfer functions currently used in APSIM

for biochar amended soils and determined that current quality modifiers that estimate biochars impact on soil water estimates were site-specific. Lastly, model simulations revealed that over 32-years, biochar applications could eliminate negative effects associated with residue harvesting, as evaluated by reduced NO_3 leaching and increased SOC levels, while not impacting corn yields (Chapter 6). Overall, biochar applications can contribute to enhancing the long-term sustainability of agro-ecosystems, but biochar age and soil type are important variables to consider.

CHAPTER 1. GENERAL INTRODUCTION

Water, food, and energy production are inherently interrelated yet until recently issues in each of these sectors have been addressed in isolation (Scott and Pasqualetti, 2010). Today there is increasing recognition of the food-water-energy nexus, which is being driven by increasing population pressure, emergent economies that are increasing demand for food, accelerating degradation of soil and water resources, and changes in global climate. One path to address nexus issues is the development of long-term sustainable agricultural practices that will support increased global food production, provide biomass for bioenergy production, help mitigate global climate change, and use freshwater more efficiently. One proposed approach to simultaneously address multiple challenges across the food-water-energy nexus is the use of biochar, the solid co-product of biomass pyrolysis, as a soil amendment (Laird, 2008**)**.

Biochar is pyrogenic, carbon-rich material intended for soil application to improve soil fertility and crop productivity while sequestering carbon (Glaser et al., 2002; Lehmann et al., 2006; Laird, 2008). Soil biochar applications have been shown to have positive impacts on crop yields and soil processes including but not limited to: soil water retention, microbial activity, greenhouse gas emissions, pollutant remediation, and nutrient leaching (Laird et al., 2010; Uchimiya et al., 2010; Kinney et al., 2012; Novak et al., 2012; Cayuela et al., 2014; Laird and Rogovska, 2015). Further, biochar is thought to be stable in soil environments for hundreds to thousands of years as evidenced by the highly fertile *terra preta* soils of the Amazonian region, which contain anthropogenic biochar with radiocarbon dates up to 6,000 YBP (Lehmann and Joseph, 2009). The stability and agronomic impacts of biochar in any given environment, however, are variable and highly site-specific, due to a complex interplay of many factors including climate, soil type, and biochar type (Verheijen et al 2010; Ippolito et al., 2012; Laird et al., 2017). Therefore, while knowledge of biochar production techniques and applications have grown immensely, knowledge gaps still exist in our understanding of biochar technology that must be investigated to develop biochar's full potential for use in agronomic and environmental systems. Two such gaps include the aging or weathering of biochars (i.e., time since incorporation into soil) and biochar impacts on plant available water (PAW) and water use efficiency (WUE).

The physical, chemical, and biological properties of biochar are known to change over time in soil environments (Downie et al., 2009). Brodowski et al. (2007) suggested that biochars are rapidly broken down into silt size or smaller particles through physical processes, whereas Kuzyakov et al. (2009) reported that biochars can persist in soils for >1000 years. Mia et al. (2017) conducted an extensive review of the available literature that discusses how biochar properties change over time. The authors reported that biochar aging occurs through multiple processes including oxidation, hydration, leaching, hydrolysis, freeze-thaw, wetting-drying, mineralization, and adsorption of dissolved organic compounds onto biochar surfaces. Biochar aging is also considered to be a two-stage process: short-term and long-term aging. Short-term aging occurs when fresh biochar is exposed to water immediately after production to prevent further combustion of the material (IBI, 2014). Long-term aging occurs after biochar application and subsequent exposure to soil and environmental processes that alter its properties (Mia et al., 2017).

Given that biochars age, studies that investigate the impacts of fresh biochars on soil and crop systems may not be relevant for assessing how biochars ultimately impact agronomic performance (Kookana, 2010) and long-term system sustainability. However, despite awareness of biochar aging mechanisms and recognition of the importance of biochar age impacts on soil environments (Seredych & Bandosz, 2007, Wang et al., 2012), the majority of studies have evaluated the effect of fresh (not aged) biochars on agronomic and environmental systems. Only a few studies have investigated how agroecosystem functions are impacted as biochars age (Major et al., 2010, Borchard et al., 2014; Rajapaksha et al., 2016).

Considerable research has shown that biochar impacts soil water retention and other soil hydrologic functions. The results of these studies are variable due to different experimental conditions including biochar and soil types, but in general these studies have found that biochar decreases bulk density and increases porosity and water retention (Novak et al., 2009; Streubel et al., 2011; Artiola et al., 2012; Basso et al., 2013; Abel et al., 2013; Rogovska et al., 2014; Ma et al., 2016). Few studies, however, have examined biochar's influence on PAW and WUE. Quantifying biochar impacts on WUE and PAW in addition to water retention is imperative because more water retained in the soil profile does not necessarily equate to more water available for growing plants (Verheijen et al., 2010). In order to achieve maximum yield potentials plants must be able to access the water retained in soils. In a period of increasing climatic variability getting "more crop per drop" (FAO, 2003) is ever more important.

In light of these gaps, this dissertation seeks to advance understanding of the impacts of biochar and biochar aging on soil properties, soil water relations, and maize yield response through a series of systematically integrated studies spanning the laboratory, greenhouse, field, and modeling scales. The main objective of each study is: study 1- develop a modified proximate analysis method to assess quality of diverse biochars for use as soil amendments; study 2- examine the influence of biochar age and type, as well as their interactions, on PAW and WUE by maize for three texturally contrasting soils; study 3- investigate the impacts of biochar,

biochar age, and cropping rotations, and their interactions, on selected soil physical and chemical properties; study 4- use long-term experimental field data to calibrate a newly developed biochar model within the Agricultural Production Systems sIMulator (APSIM) cropping systems model and apply the model to determine the optimum biochar application rate for Midwest maize bioenergy cropping systems under different management scenarios; and study 5- evaluate the applicability of pedotransfer functions, which use soil organic matter content and texture to estimate soil water parameters, for soils with and without biochar amendments and improve the soil water equations used in the APSIM biochar model to account for biochar carbon.

References

Abel, S., Peters, A., Trinks, S., Schonsky, H., Facklam, M., Wessolek, G., 2013. Impact of biochar and hydrochar addition on water retention and water repellency of sandy soil. Geoderma 202-203, 183-191. http://dx.doi.org/10.1016/j.geoderma.2013.03.003.

Artiola, J.F., Rasmussen, C., Freitas, R., 2012. Effects of a biochar-amended alkaline soil on the growth of romaine lettuce and bermuda grass. Soil Sci. 177, 561-570. http:// dx.doi.org/10.1097/SS.0b013e31826ba908.

Basso, A.S., Miguez, F.E., Laird, D.A., Horton, R., Westgate, M., 2013. Assessing potential of biochar for increasing water-holding capacity of sandy soils. GCB Bioenergy 5(2), 132-143. http://dx.doi.org/10.1111/gcbb.12026.

Borchard, N., Siemens, J., Ladd, B., Möller, A., Amelung, W., 2014. Application of biochars to sandy and silty soil failed to increase maize yield under common agricultural practice. Soil Tillage Res. 144, 184-194. doi.org/10.1016/j.still.2014.07.016.

Brodowski, S., Amelung, W., Haumaier, L., and Zech, W., 2007. Black carbon contribution to stable humus in German arable soils. Geoderma 139, 220-228.

Cayuela, M.L., van Zwieten, L., Singh, B.P., Jeffery, S., Roig, A., Sanchez-Monedero, M.A., 2014. Biochar’s role in mitigating soil nitrous oxide emissions: a review and meta-analysis, Agric. Ecosyst. Environ. 191, 5-16. http://dx.doi.org/10.1016/j.agee.2013.10.009

Downie, A., Crosky, A., Munroe, P., 2009. Physical properties of biochar. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management: Science and Technology. Earthscan, London, UK, pp. 13–32.

Food and Agriculture Organization of the United Nations (FAO), 2003. More crop per drop: the role of agriculture is essential in resolving the world's water problems. http://www.fao.org/english/newsroom/focus/2003/water.htm, Accessed date: 9 January 2017.

Glaser, B., Lehmann, J., Zech, W., 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal-a review. Biol. Fertil. Soils 35, 219-230.

International Biochar Initiative (IBI), 2014. Standardized product definition and product testing guidelines for biochar that is used in soil. In: Report Version 2.0 IBI Biochar Standards.

Ippolito, J.A., Laird, D.A., Busscher. W.J., 2012. Environmental Benefits of Biochar. J. Environ. Qual. 41. doi:10.2134/jeq2012.0151

Kinney, T.J., Masiello, C.A., Dugan, B., Hockaday, W.C., Dean, M.R., Zygourakis, K., Barnes, R.T., 2012. Hydrologic properties of biochars produced at different temperatures. Biomass Bioenergy 41, 34-43.

Kookana, R., 2010. The role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils: a review. Aust. J. Soil Res. 48, 627–637.

Kuzyakov, Y., Subbotina, I., Chen, H., Bogomolova, I., Xu, X., 2009. Black carbon decomposition and incorporation into soil microbial biomass estimated by C-14 labeling. Soil Biology & Biochemistry. 41, 210–219.

Laird, D.A., Rogovska, N., 2015. Chapter 18: Biochar effects on nutrient leaching, in J. Lehmann, S. Joseph (Eds.). Biochar for environmental management-science, technology and implementation. London, New York: Earthscan, 519-540.

Laird, D.A., 2008. The charcoal vision: A win‑win‑win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. Agron. J. 100, 178‑181. doi:10.2134/agrojnl2007.0161

Laird, D.A., Fleming, P., Davis, D.D., Horton, R., Wang, B., Karlen, D.L., 2010. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. Geoderma 158, 443-449. http://dx.doi.org/10.1016/j.geoderma.2010.05.013.

Laird, D.A., Novak, J.M., Collins, H.P., Ippolito, J.A., Karlen, D.L., Lentz, R.D., Sistani, K.R., Spokas, K., Van Pelt, R.S., 2017. Multi-year and multi-location soil quality and crop biomass yield responses to hardwood fast pyrolysis biochar. Geoderma 289, 46-53. doi.org/10.1016/j.geoderma.2016.11.025

Lehmann, J., Joseph, S., 2009. Biochar for Environmental Management: Science and Technology. Earthscan, London, UK.

Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems- a review. Mitigation and Adaptation Strategies for Global Change. 11, 403-427.

Ma, N., Zhang, L., Zhang, Y., Yang, L., Yu, C., Yin, G., Doane, T., Wu, Z., Zhu, P., Ma, X., 2016. Biochar improves soil aggregate stability and water availability in a mollisol after three years of field application. PLoS ONE 11 (5), e0154091. http://dx.doi.org/ 10.1371/journal.pone.0154091.

Major, J., Rondon, M., Molina, D., Riha, S.J., Lehmann, J., 2010. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. Plant Soil 333, 117-128.

Mia, S., Dijkstra, F.A., Singh, B., 2017. Long-term aging of biochar: a molecular understanding with agricultural and environmental implications. Adv. Agron. 141, 1-51. http://dx.doi.org/10.1016/bs.agron.2016.10.001.

Novak, J.M., Lima, I., Xing, B., Gaskin, J., Steiner, C., Das, K., Ahmedna, M., Rehrah, D., Watts, D.W., Busscher, W.J., Schomberg, H., 2009. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. Ann. Environ. Sci. 3, 195-206.

Novak, J.M., Busscher, W.J., Watts, D.W., Amonette, J.E., Ippolito, J.A., Lima, I.M., Gaskin, J., Das, K.C., Steiner, C., Ahmedna, M., Rehrah, D., Schomberg, H., 2012. Biochars impact on soil-moisture storage in an ultisol and two aridisols. Soil Science 177, 310-320.

Rajapaksha, A.U., Chen, S.S., Tsang, D.C.W., Zhang, M., Vithanage, M., Mandal, S., Gao, B., Bolan, N.S., Ok, Y.S., 2016. Engineered/designer biochar for contaminant removal/ immobilization from soil and water: potential and implication of biochar modification. Chemosphere 148, 276-291.

Rogovska, N., Laird, D.A., Rathke, S.J., Karlen, D.L., 2014. Biochar impact on Midwestern mollisols and maize nutrient availability. Geoderma 230-231, 340-347. http://dx. doi.org/10.1016/j.geoderma.2014.04.009.

Scott, C., Pasqualetti, M., 2010. Energy and Water Resources Scarcity: Critical Infrastructure for Growth and Economic Development in Arizona and Sonora. Natural Resources J. 50, 645-682.

Seredych, M., Bandosz, T.J., 2007. Mechanism of ammonia retention on graphite oxides: role of surface chemistry and structure. J. Phys. Chem. C 111, 15596-15604.

Streubel, J.D., Collins, H.P., Garcia-Perez, M., Tarara, J., Granatstein, D., Kruger, C.E., 2011. Influence of contrasting biochar types on five soils at increasing rates of application. Soil Sci. Soc. Am. J. 75, 1402-1413.

Uchimiya, M., Chang, S., Klasson, K.T., 2011. Screening biochars for heavy metal retention in soil: role of oxygen functional groups. J. Hazard. Mater. 190, 432-441.

Verheijen, F., Jeffery, S., Bastos, A.C., van der Velde, M., Diafas, I., 2010. Biochar application to soils: a critical scientific review on effects on soil properties processes and functions. In: Joint Research Center (JRC), Scientific and Technical Report. Office for the Official Publications of the European Communities, Luxemberg.

Wang, J., Pan, X., Liu, Y., Zhang, X., Xiong, Z., 2012. Effects of biochar amendment in two soils on greenhouse gas emissions and crop production. Plant Soil 360, 287-298.

CHAPTER 2. MODIFIED METHOD FOR PROXIMATE ANALYSIS OF BIOCHARS

Modified from a manuscript published in the Journal of Analytical and Applied Pyrolysis

Deborah Aller[1], Santanu Bakshi[1], David A. Laird[1]

Abstract

Proximate analysis is widely used to determine moisture, volatile matter (VM), fixed carbon (FC) and ash content of biochars. The original ASTM D1762-84 method was developed to assess quality of hardwood charcoal for use as fuel. We have developed a modified proximate analysis method to assess quality of diverse biochars for use as soil amendments. We determined that a N_2 purge is necessary during both moisture and VM determination to avoid errors associated with sample oxidation. We assessed a range of boundary temperatures (350-950°C) for separating VM and FC, and determined that 800°C is the minimum temperature required to distinguish between VM and FC in biochars. Furthermore, correlation between VM/FC and molar H/C_{org} ratios suggests that VM/FC ratios are a useful measure of biochar stability. Use of the proposed modified method is encouraged to reduce variance in analytical results among studies.

Keywords: Proximate analysis, Volatile matter, Fixed carbon, N_2 purge, Biochar stability, VM/FC ratio

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Introduction

Proximate analysis, American Society for Testing and Materials (ASTM) method number D1762-84, was originally developed for analysis of wood charcoal [1]. More recently, however, this method has been utilized for assessing quality of biochar, the solid co-product of thermochemical conversion of biomass to bioenergy, which is applied to soils to enhance soil quality and sequester carbon. Proximate analysis provides basic characterization information about biochars including moisture, volatile matter (VM), fixed carbon (FC) and ash content. Ash content is related to liming value and inorganic element content of biochar [2], while VM and FC have been used to estimate the labile and recalcitrant biochar fractions, respectively [3].

Biochars have many unique properties relative to charcoal. Most charcoals are produced from hardwood feedstocks by slow pyrolysis and are marketed in either lump or briquette forms for use as a fuel. Biochars, on the other hand, are produced from both wood and herbaceous feedstocks such as, corn stover, rice husks, sugarcane bagasse, and switchgrass, using various thermochemical conversion technologies, including slow pyrolysis, fast pyrolysis and gasification. Biochars are intended for use as soil amendments and vary widely in particle size, chemical composition and porosity; hence their impacts on agro-ecosystems can be highly variable [4].

Several factors influence the physical and chemical properties of biochars. Brewer et al. [5] conducted an extensive biochar characterization study and reported that the chemical and physical properties of biochar differ depending on both production technique and biomass feedstock. Other studies indicate that biochar properties change over time (weathering or aging) in soil environments [6, 7] and thus both fresh and aged biochars must be studied [8-10]. Lastly, Bradbury and Shafidazeh [11] reported weight gain by biochar during moisture determination using standard oven drying techniques, implying O_2 chemisorption on biochar surfaces. The diversity of biochar properties relative to charcoal and the evidence for chemisorption of O_2 on biochar surfaces suggest a need to evaluate the reproducibility and/or utility of results obtained using the ASTM proximate analysis method for biochars.

The ASTM method stipulates that crucibles and lids be heated to 750°C, cooled, and weighed prior to their use for proximate analysis. Samples are initially sieved to 850 µm, then moisture content is determined as the percent mass loss on heating air-dry samples to 105°C in an air atmosphere, VM as percent mass lost between105°C and 950°C, and percent ash as mass remaining after combustion at 750°C for 6 h. During VM determination the ASTM method prescribes a process of preheating the furnace to 950°C, preheating the samples in crucibles (lids-on) by placing them on the outer edge of the furnace with the door open for two minutes at 300°C, then moving them a little farther into the furnace with the door open for three minutes at 500°C, and finally placing the crucibles at the back of the furnace with the door closed for six minutes.

We consider the ASTM procedure to be problematic because the samples may be exposed to O_2 during both the moisture and VM determination steps. Furthermore, the ASTM VM procedure is not well controlled, as heating is not necessarily the same in all furnaces when the door is open, and moving samples around in a hot furnace limits the number of samples that can be analyzed at the same time, and is potentially hazardous.

Many biochar research groups have chosen to modify the ASTM proximate analysis method [5,8,12-18]. None of these researchers, however, have systematically investigated the effects of method modifications on the results. Following is a brief discussion of modified proximate analysis procedures used by Mitchell et al. [12] and Enders et al. [13], which were chosen to emphasize the variability of procedures used for proximate analysis found in the literature.

Mitchell et al. [12] utilized thermogravimetric analysis (TGA) for proximate analysis of biochars. Moisture content was estimated as percent of sample mass lost between room temperature and 100°C, VM as percent mass lost between 150°C-450°C, ash as per-cent mass remaining after the 750°C combustion, and %FC as one hundred minus %moisture, %ash, and %VM. During the TGA procedure, samples were heated under a N_2 atmosphere to 750°C, then air was introduced into the system and maintained for four minutes to facilitate combustion. The use of a N_2 purge for both moisture and VM determination should preclude weight gain due to chemisorption of O, but the 450°C boundary temperature for VM determination has not been validated with diverse biochars. Other potential problems with the Mitchell et al. [12] method are a small samples size, which can decrease analytical precision, and the fact that many laboratories do not have access to a TGA instrument.

A detailed description of the modified procedure of Enders et al. [13] is provided in their supplementary material but in short, crucibles + covers were heated to 750°C and cooled to ensure no moisture was present prior to analysis. Moisture content was determined in an argon rich atmosphere as mass lost after 18 h at 105°C. Percent VM was determined without argon after heating the furnace to 950°C, opening the door to put crucibles in the furnace, leaving samples for 10 min, and then removing and letting samples cool. Ash content was determined as mass remaining after 6 h at 750°C in air. The authors highlighted that during VM determination the furnace cooled off when the door was opened and did not reach 950°C again for eight minutes. Although covers were on the crucibles during VM determination to reduce exposure to

O_2, opening the door introduced a large amount of oxygen into the furnace, increasing the potential for partial ashing of the samples.

The many variations of the proximate analysis method used by researchers is problematic for the biochar research community as the lack of an accepted standard protocol limits comparisons of results between studies. Proximate analysis is an important biochar characterization method because it is quick, easy, and relatively inexpensive and because it provides an estimation of the size of the ash, VM and FC fractions in biochars. Assuming that VM and FC are indirect measures of the labile and recalcitrant biochar fractions, the results of proximate analysis are useful for predicting the impact of biochar amendments on soil properties and the long-term stability of biochar C in soil environments.

The goal of this study was to develop a modified proximate analysis procedure for biochars that is accurate, reproducible and simple. Specifically, we seek to develop a procedure that can be used with diverse biochar samples, reduces sample handling during the procedure (relative to the ASTM method), allows many samples to be analyzed at the same time and yields results which are relevant for assessing biochar C stability in soils.

Materials and Methods

The source and abbreviations for the 22 biochars used in this study are listed in supporting materials (Table S1). Details of the production, collection, weathering and corresponding chemical and physical properties of the biochars are described elsewhere [7]. In brief, 6 un-weathered (Fresh-1), 6 laboratory-weathered (LW),[1] 5 un-weathered but stored

[1] Laboratory-weathered (LW) and field-weathered (FW) are equivalent to Laboratory-aged (LA) and Field-aged (FA), respectively as found in Bakshi et al. [7].

(Fresh-2), and 5 field-weathered (FW)[1] biochars were investigated. These biochars were variously produced by fast pyrolysis, slow pyrolysis and gasification techniques from five different biomass feedstocks (corn stover, soybean residue, hardwood, switchgrass and macadamia nut shell). The controlled chemical aging procedure for the six LW biochars (particle size <1 mm) included a one month incubation at 40°C in a 1 M HCl solution with weekly additions of 30% H_2O_2, followed by Ca-saturation, and then another one month incubation at 40°C in an aqueous solution containing dissolved organic carbon (compost tea). The five field weathered biochars were originally applied to experimental field plots in Minnesota and South Dakota in 2008 and 2011, respectively, and were collected and separated from soil in 2014. Initial bulk soil samples (0-20 cm depth) were air-dried and sieved (44 mm) to remove large biochar particles. Secondary sieving to separate smaller biochar particles occurred by wet sieving (0.045 mm) and hand picking. All field weathered biochar was subsequently ground using a mortar and pestle to a particle size of <1 mm and stored in sealed containers [7]. H and C_{org} content of the various biochars was determined using a combustion analyzer (Vario Microcube, Elementar Analysensysteme GmbH) after the samples had been ball milled to reduce particle size and treated for 24 h with 0.05 mol L^{-1} HCl to remove carbonates [7].

Modified Proximate Analysis Method

Moisture content of samples was determined based on mass loss after two hours at 105°C under N_2 purge. Approximately 0.5 g of air-dried biochar was weighed into a ceramic crucible ($M_{initial-BC}$).The samples were placed inside of a Lindberg muffle furnace (model 51442), which was initially purged with N_2 gas for ≥25 min at a flow rate of 6 L min^{-1}, equivalent to roughly 10 furnace volumes, to ensure removal of all oxygen. During the subsequent heating phase the furnace was purged with N_2 at a flow rate of 3 L min^{-1}. After the 2 h heating, the furnace was turned off and samples were transferred immediately to a desiccator, left to cool for one hour, and then weighed.

Volatile matter was determined by heating the oven dry samples under N_2 purge to various potential VM/FC separation temperatures. To determine the appropriate VM/FC separation temperature, samples were heated at 2°C min^{-1} to each of nine different temperatures: 350°C, 550°C, 650°C, 700°C, 750°C, 800°C, 850°C, 900°C, and 950°C. During heating, the crucibles containing the biochar were covered with ceramic lids, placed in a stainless steel box inside of a muffle furnace (Thermo Scientific Lindberg/Blue M Box Furnace BF51894C-1). A N_2 purge line and thermocouple were inserted through the top of the furnace and down into the stainless steel box through a small hole in the box cover. The box was purged with N_2 gas for ≥15 min at a flow rate of 6 L min^{-1} (approximately 10 box volumes). After the initial purge, the N_2 flow rate was decreased to 3 L min^{-1}, the furnace was set to the desired peak separation temperature, and turned on. The temperature inside of the stainless steel box was measured every 60 s during the heating treatments. Once the temperature inside of the stainless steel box reached the desired VM/FC separation temperature, the furnace was switched off and furnace door opened. The N_2 purge inside the stainless steel box was maintained (3 L min^{-1}) during cool down (2-4 h), after which the crucibles were weighed to determine the mass of FC + Ash ($M_{FC + Ash}$) after subtracting the empty crucible weight.

Ash content of biochars was determined by heating the same samples to 730°C in an air atmosphere using the same muffle furnace. To ensure complete combustion, crucible lids were removed and a low flow of house air (1.5 L min^{-1}) was constantly flushed through the furnace. The furnace was heated to 730°C and held at that temperature overnight (8-10 h). After ashing, the furnace was switched off and allowed to cool for one hour before the samples were transferred to a desiccator to cool. The crucibles were weighed and ash mass (M_{ash}) was determined by subtracting the empty crucible weight.

All reported proximate analysis data in this manuscript are the arithmetic mean of triplicate measurements.

Proximate Analysis Calculations

The percent moisture (% Moisture) and percent ash (% Ash) were determined using Eq. (1) and (2), respectively.

$$\% \, Moisture = \left(\frac{(\mathrm{M}_{initial} - M_{OD-BC})}{M_{OD-BC}}\right) * 100 \tag{1}$$

$$\% \, Ash = \left(\frac{M_{ash}}{M_{OD-BC}}\right) * 100 \tag{2}$$

where $M_{initial}$ is the initial sample mass in grams , M_{OD-BC} is the mass in grams of the sample after oven drying at 105 °C under an N_2 purge, and M_{ash} is the sample mass in grams after combustion at 730 °C overnight.

The percent volatile matter (%VM) and percent ash free volatile matter (% $VM_{ash-free}$) were determined using Eqs. (3) and (4), respectively.

$$\% \, VM = \left(\frac{M_{OD-BC} - M_{FC+Ash}}{M_{OD-BC}}\right) * 100 \tag{3}$$

$$\% \, VM_{ash-free} = \left(\frac{M_{OD-BC} - M_{FC+Ash}}{M_{OD-BC} - M_{ash}}\right) * 100 \tag{4}$$

where M_{FC+Ash} is the mass in grams of fixed carbon and ash in the sample.

The percent fixed carbon (%FC) and percent ash free fixed carbon (% $FC_{ash\text{-}free}$) were determined using Eqs. (5) and (6), respectively, as previously described by Ronsse et al. [19].

$$\%FC = \left(\frac{(M_{FC+ash} - M_{ash})}{(M_{OD-BC})}\right) * 100 \tag{5}$$

$$\%FC_{ash-free} = \left(\frac{(M_{FC+ash} - M_{ash})}{(M_{OD-BC} - M_{ash})}\right) * 100 \tag{6}$$

Statistical Analysis

All analyses were carried out in SAS 9.4 (SAS Institute Inc., 2013), with statistical significance accepted at the 5% significance level. An initial t-test was conducted to determine whether results differed between the ASTM method and the Modified method. A significant method by biochar type interaction was found ($P < 0.05$). Analysis of variance (ANOVA) was subsequently conducted to assess differences between methods on each individual biochar type, with biochar type referring to the production technique, feedstock, and weathering treatments (Fresh-1, LW, Fresh-2, FW) of the 22 different biochars used in this study.

Results and Discussion

Assessment of Moisture and Ash Contents

The moisture content of the 22 diverse biochars varied substantially and was influenced by the degree of weathering (Fig. 1). Overall the LW biochars had significantly higher moisture content than Fresh-1, Fresh-2, and FW biochars with the exception of FW HS2 and both Fresh-2 and FW MNS ($P < 0.05$). This may have resulted from the intensive oxidation and acidification treatments, which transformed the surfaces of the LW biochars from being hydrophobic to hydrophilic, by the incomplete drying of the LW biochars prior to storage, and/or the absorption of moisture during storage. Furthermore, there was generally more variability in moisture content of the LW biochars than the Fresh-1, Fresh-2, and FW biochars. This suggests non-homogeneity in moisture content among biochar subsamples taken from the storage containers.

Statistical analysis of the moisture content data indicated a significant biochar type by method interaction ($P < 0.05$). The results indicate that the ASTM and Modified methods gave different results for moisture content in 9 of the 22 biochars, and that differences in moisture content values determined by the two methods are not consistent but rather influenced by biochar feedstock, weathering, and production technique (Fig. 1).

The Modified method indicated higher moisture levels than the ASTM method for all six of the Fresh-1 biochars, with these values significantly higher in five of the six biochars ($P < 0.05$). Fresh-1 CF was the only biochar found to be not significantly different for moisture content between the two methods ($P = 0.064$). For both methods moisture content is determined by heating the samples to 105°C for 2 h, with the key difference between the methods being use of an N_2 purged atmosphere in the Modified method and an air atmosphere in the ASTM method. Exposure to O_2 during heating to 105°C could cause weight loss if thermally labile organic compounds are fully oxidized to CO_2 and/or H_2O. Alternatively, exposure to O_2 during heating to 105°C could cause weight gain if O_2 is chemisorbed on biochar surfaces, due to partial rather than complete oxidation of biochar C. The Fresh-1 biochars were produced a few weeks prior to analysis and stored in sealed containers, thus they had minimal exposure to atmospheric O_2, moisture, and other environmental conditions between production and analysis. Our results (Fig. 1) suggest that chemisorption of O_2 significantly reduced the weight loss (apparent moisture content as determined by the ASTM method relative to the Modified method) for five of the six Fresh-1 biochars. Indeed, two of the Fresh-1 biochars had significant “negative” moisture content (i.e., weight gain during heating to 105°C in air) as determined by the ASTM method (Table S2), which is strong evidence of O_2 chemisorption.

In contrast with the results for the Fresh-1 biochars, there were no significant differences in measured moisture content between the two methods for the 5 Fresh-2 biochars, with the exception of Fresh-2 SG ($P = 0.0008$). We do not know details of storage conditions for the Fresh-2 biochars, but we do know that they were stored for >3 years, and based on the results (Fig. 1) it appears that these samples were variously exposed to O_2 and moisture during storage, which may have limited the potential for chemisorption of O_2 during heating.

The results are variable among the LW and FW biochars; 2 samples showed higher moisture content by the ASTM method, 1 showed higher moisture content by the Modified method, and 8 showed no significant difference in moisture content between the methods (Fig. 1). Again we attribute these differences to the exposure to O_2 that occurs during drying in the ASTM method but not the Modified method. Lower apparent moisture levels by the ASTM method than the Modified method again implies chemisorption of O_2. Higher apparent moisture levels by the ASTM method than the Modified method indicates mass loss as either CO_2 or other volatile compounds. Both the LW and FW biochars had an opportunity to adsorb biogenic dissolved organic compounds (DOC) during aging [7], hence it is possible that differences in apparent moisture content determined by the ASTM and Modified methods are related to the presence of thermally labile biogenic organic compounds adsorbed on the surfaces of the LW and FW biochars.

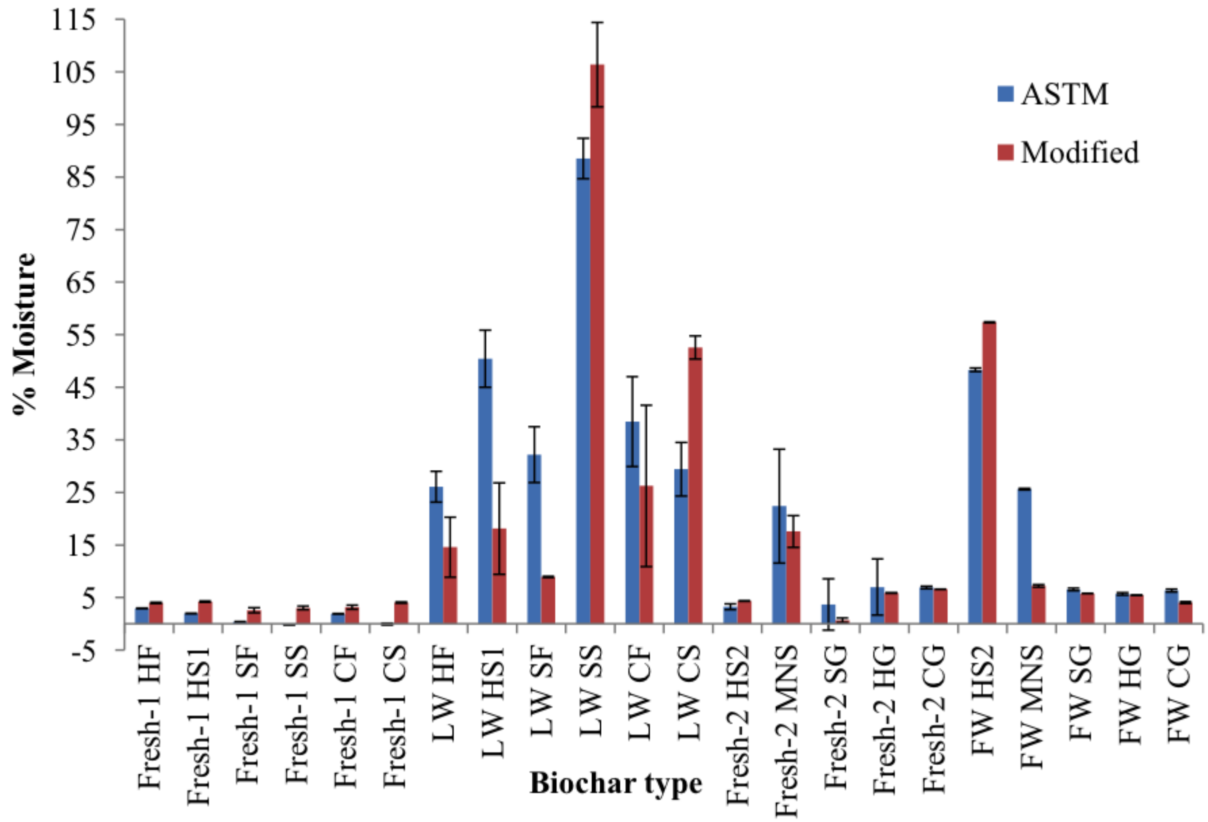


Fig. 1. Percent moisture loss determined after two hours at 105°C for all biochars. An N_2 purge was used with the Modified method but not with the ASTM method. Error bars represent one standard error of the mean.

The hydrophobicity of biochar surfaces and the degree of biochar weathering influence the ability of biochars to absorb water from an atmosphere or solution and the amount of water held by biochars when they are air dried. The lack of uniformity across biochars in retaining water has the potential to impact proximate analysis results. This highlights the need to standardize the reporting of proximate analysis moisture, VM, FC, and ash content data based on the oven dry weight of biochars. Additionally, any inaccuracy in determining the oven dry weight will impact the accuracy of subsequent determinations of VM, FC, and ash content of biochars. Our results for moisture determination (Fig. 1) emphasize the importance of determining moisture content of biochars in an atmosphere absent of O_2. The use of a N_2 purge in the Modified procedure prevented both complete oxidation of organic compounds to CO_2 and the chemisorption of O_2 onto biochar surfaces.

Both methods indicated similar estimates of ash content for 16 of the 22 biochars. Measured ash content values differed between methods for the Fresh-1 HF, Fresh-1 SF, Fresh-1 SS, LW HF, LWSF, and FW CG biochars (Fig. 2). There are no obvious connections between these six biochars that explain the divergent results. Moreover, two of these biochars were found to have higher ash content and four to have lower ash content as determined by the ASTM method relative to the Modified method. The protocols for determining ash content are similar for both methods, although in the Modified method a small amount of house air is constantly introduced into the furnace during ashing to ensure an adequate supply of O_2 for complete combustion. With the ASTM method we observed that some biochar particles were resistant to oxidation, especially when encrusted in ash. Hence, incomplete combustion could explain the higher ash content measured by the ASTM method for two of the samples but not the lower ash content measured by the ASTM method for the four other samples relative to ash content measured by the Modified method. Differences in the extent of thermal degradation of mineral phase [15,20], is another possible explanation for the observed differences in biochar ash content determined by the two methods. It is tempting to attribute these differences to sampling error and/or lack of homogeneity in the stored biochar samples, however, the ash analysis was determined in triplicate and standard errors are small relative to the difference between the methods for these six samples (Fig. 2). Overall, to ensure that all carbon is oxidized we recommend ashing samples at 730°C for an 8-10 h period with a constant low flow of air, to supply O_2.

Evaluation of VM, FC, and the VM/FC Separation Temperature Boundary

Standardizing the method for determining VM and FC was a key objective of this study. To do so, we evaluated nine different VM/FC separation temperatures all under N_2 purge to preclude any mass loss or gain due to oxidation. Our results indicate that mass loss on heating increased rapidly for all biochars between 350°C-650°C, slowly between 650°C-800°C, and then stabilized at and above 800°C (Fig. S1). Furthermore, the lack of change in apparent VM/FC ratios relative to VM/FC ratios determined for a 950°C separation temperature supports 800°C as the minimum temperature that should be used to determine VM content of biochars, although this does not preclude the use of higher temperatures (Fig. S2).

The importance of using an inert gas purge during VM determination is evident by comparing the %VM results determined by the ASTM protocol and the Modified method using the 800°C VM/FC separation temperature (Fig. 3). Overall, %VM differed for 16 of the 22 biochars between the two methods ($P < 0.05$). Estimates of %VM obtained with the ASTM method were significantly higher for all of the Fresh-1 and LW biochars except for LW HS1 and LW SS relative to the Modified method. By contrast, variable results were obtained for the Fresh-2 and FW biochars, with %VM being higher when determined by the ASTM method for biochars produced by slow pyrolysis and lower for biochars produced by gasification relative to VM determined by the Modified method. These differences are influenced to some extend by the inaccurate estimates of oven dry weights and moisture content obtained by the ASTM method, however, we primarily attribute the opposing trends to exposure to O_2 during VM determination by the ASTM method. The ASTM method relies on loose fitting lids on the crucibles and the release of volatile compounds from the sample to keep O_2 away from the sample during heating for VM determination. With the ASTM protocol some sample exposure to O_2 is inevitable. By contrast the Modified method uses a thorough N_2 purge to preclude exposure of the samples to O_2 during heating and cooling of samples. Our data suggest that a substantial amount of mass was lost (presumably as CO_2 and H_2O) from the fast and slow pyrolysis biochars due to oxidation by O_2 that leaked into the crucibles under the ASTM protocol. The greater aromaticity of gasification biochars likely resulted in only partial oxidation rather than complete oxidation and hence chemisorption of O_2. This suggests that among the gasification biochars competing reactions which have a counter balancing effect are simultaneously taking place. The substantial differences between %VM determined by the ASTM and Modified methods (Fig. 3) highlight the importance of using an inert gas purge when determining VM of biochars.

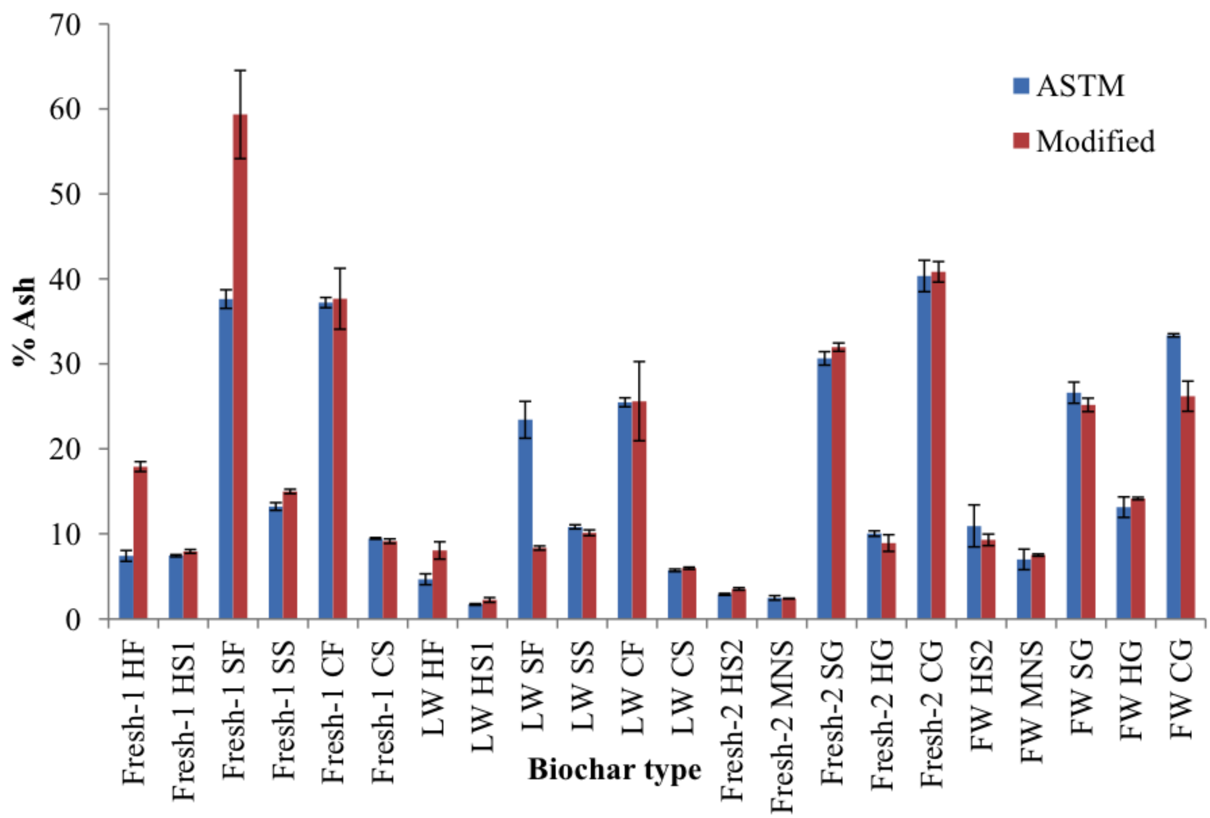


Fig. 2. Percent ash content of all biochars determined by the ASTM and modified methods. Error bars represent one standard error of the mean.

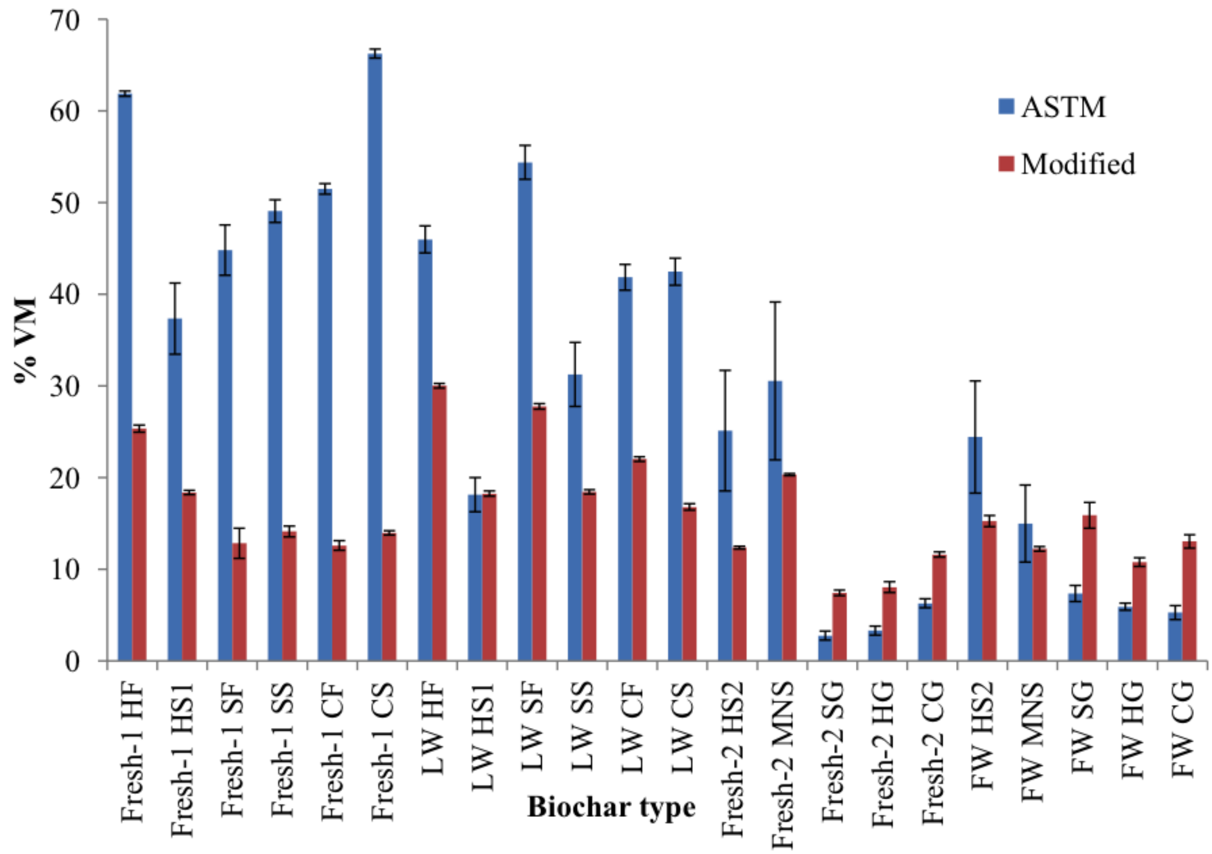


Fig. 3. Percent volatile matter of all biochars determined by the ASTM and modified methods. Error bars represent one standard error of the mean.

Percent FC values determined by the ASTM method differed ($P < 0.05$) from %FC values determined by the Modified method in 16 of 22 biochars (Fig. 4); revealing the exact opposite pattern as seen in %VM (Fig. 3). Specifically, %FC was lower when determined by the ASTM method for all fast and slow pyrolysis biochars with the exception of LW HS1, which was not significantly different. In contrast, the ASTM method indicated higher %FC values for the gasification biochars than the Modified method (Fig. 4). We again attribute these large differences in %FC between the two methods to exposure to O_2 during VM/FC determination following the ASTM protocol and differing levels of oxidation of biochar C.

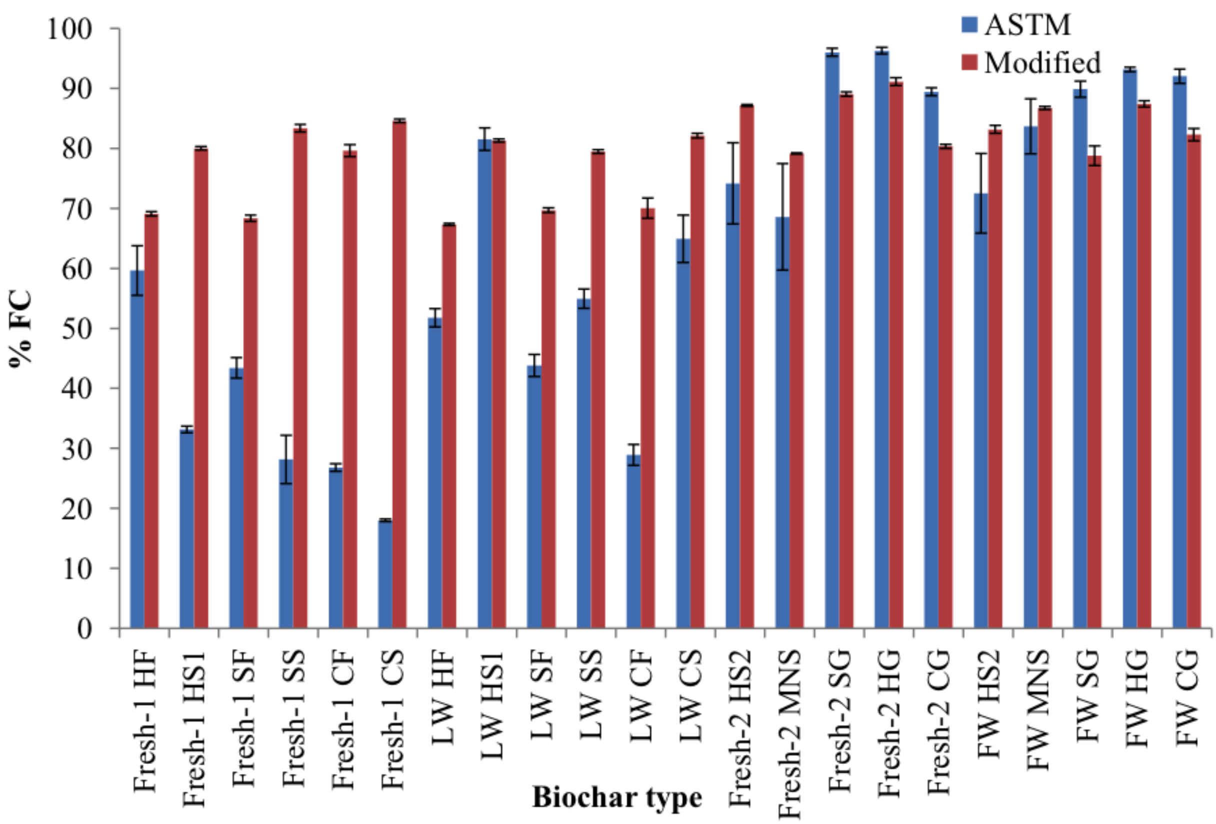


Fig. 4. Percent fixed carbon (dry ash free) of all biochars for the ASTM and modified methods. Error bars represent one standard error of the mean.

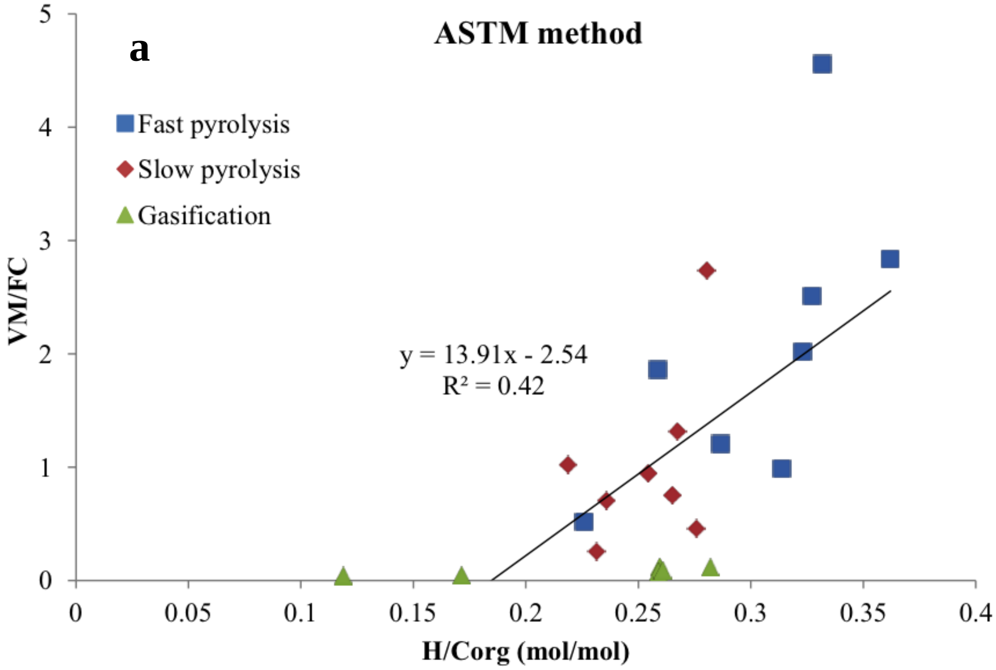
Assessment of Proximate Analysis as a Method to Measure Biochar C Stability

The ability to accurately estimate biochar C stability is critical to advance biochar utilization. Currently, the International Biochar Initiative (IBI) recommends the use of the molar H/C_{org} ratio as an index of biochar C stability [13,21]. The H/C_{org} ratio is also an index of biochar aromaticity as H is only bonded with C atoms on the edges of condensed aromatic C (graphitic) sheets. Thus the more disordered the biochar C structure, the more H it will contain and in theory the greater the rate of biochar degradation in soil environments. Elemental analysis of H and C content of biochars requires access to a thermal combustion instrument, which many laboratories do not have. Proximate analysis has the potential to be a less expensive and more widely available method for assessing biochar C stability and overall biochar quality, and hence provide useful input parameters into cropping systems models.

Previous work has reported a relatively strong correlation between %VM and O:C elemental ratios of biochar but no evidence of a correlation between %VM and estimated half-life of biochar C [22]. For this reason, the IBI did not recommend the use of %VM as an index of biochar C stability [21]. Percent VM, however, is strongly influenced by ash content [%VM = VM × 100/(VM + FC + Ash)], which is more a function of feedstock quality than pyrolysis technology and peak pyrolysis temperature. Furthermore, our results (Fig. 3) demonstrate that %VM is highly dependent on proximate analysis methodology and that the ASTM method can both over and under estimate %VM. However, previous work did not consider the importance of methodology used in evaluating proximate analysis data for assessing biochar C stability. Here we compared VM/FC ratios determined by the ASTM and Modified methods with H/C_{org} ratios determined by thermal combustion analysis. VM/FC ratios are independent of ash content and hence a more robust index of biochar C stability than %VM.

The VM/FC ratios determined by both the ASTM and Modified methods are correlated (R^2= 0.42 and 0.62, respectively) with the H/C_{org} ratios (Fig. 5a and b). The VM/FC ratios determined by the ASTM method are an order of magnitude higher ($P < 0.05$) for all fast and slow pyrolysis biochars compared to VM/FC ratios determined by the Modified method. By contrast, the VM/FC ratios for all the gasification biochars were lower when determined by the ASTM method than the Modified method. This is attributed to the opposing responses of the pyrolysis and gasification biochars to the exposure to limited O_2 during VM determination in the ASTM method. As discussed previously, our data suggest that during the ASTM procedure the fast and slow pyrolysis biochars had greater mass lost as volatiles compared to the Modified method due to complete oxidation (presumably as CO_2 and H_2O) whereas the gasification biochars had lower mass lost as volatiles under the ASTM method than the Modified method as a result of partial oxidation (chemisorption of O_2).

In developing the Modified method, we considered the relationship between VM/FC and H/C_{org} ratios for potential VM/FC separation temperatures ranging from 350 to 950°C (Fig. S3). For VM/FC separation temperatures greater than 650°C, the VM/FC and H/C_{org} ratios of the studied biochars are correlated and show similar distributions for the fast pyrolysis, slow pyrolysis and gasification biochars. The gasification biochars have relatively low H/C_{org} and VM/FC ratios, which is consistent with greater condensation into polyaromatic C structures. The fast pyrolysis biochars have relatively high H/C_{org} and VM/FC ratios, which is consistent with more single ring aromatic structures and/or the condensation of volatile aliphatic compounds into the biochars during fast pyrolysis. The slow pyrolysis biochars are clustered in the middle between the fast pyrolysis and gasification biochars on the H/C_{org} and VM/FC plots. These data suggest that the H/C_{org} and VM/FC ratios are related measures of stability but are not identical. Differences between the two indices of biochar stability are attributed to the inherent differences among biochars which result from the use of various feedstocks and biochar production techniques. These findings suggest that VM/FC ratios as determined by the Modified proximate analysis method have relevance for assessing the long-term stability of biochar C in soils. Specifically, %VM when measured using an inert gas purge, which avoids problems with partial or complete oxidation, is by definition a measure of the mass of the thermally labile biochar fraction. Further research is needed to determine whether or not the thermally labile fraction is comparable to the biologically labile biochar fraction.



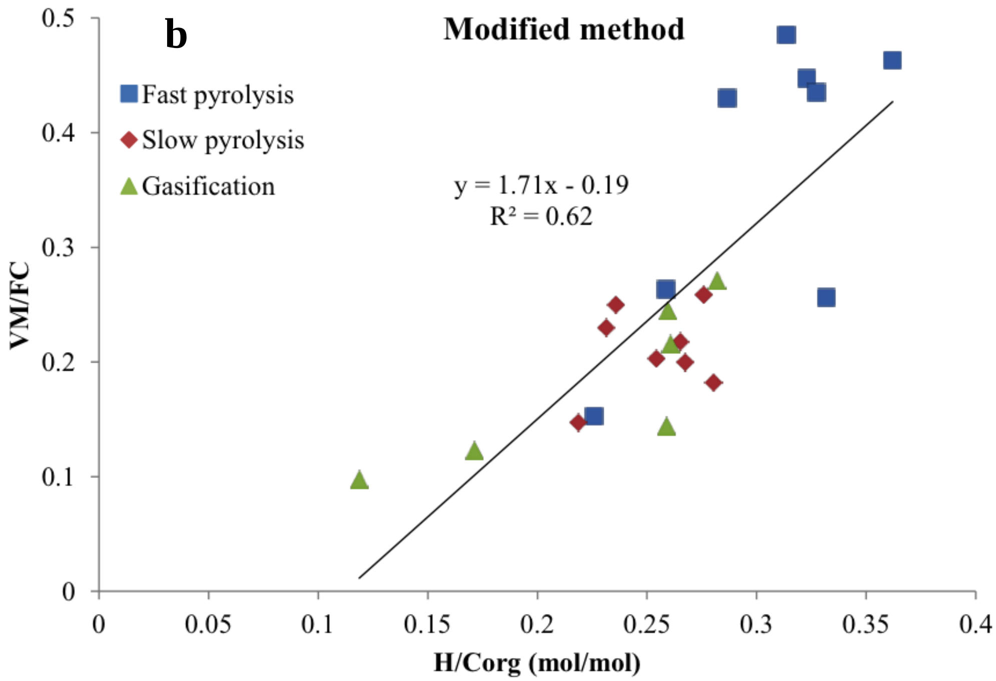


Fig. 5. Volatile matter/fixed carbon (VM/FC) vs. H/C_{org} (mol:mol) ratios for all biochars grouped by production technique; (a) VM and FC were determined using the ASTM method; (b) VM and FC determined by our modified method using 800°C.

Conclusions

Significant differences were found between the ASTM method and Modified method. Results from our Modified method support its appropriateness for use in the proximate analysis of biochars and for VM/FC ratios to assess biochar C stability and quality. The Modified method accommodates a large sample size, reduces sample handling and potential hazards, is applicable for diverse biochars, and avoids errors caused by oxidation, which are inherent to the ASTM method. A standard proximate analysis protocol designed specifically with biochar diversity in mind will minimize differences in results among studies and facilitate the greater comparison of biochar properties between researchers.

Acknowledgments

This work was made possible by the Agriculture and Food Research Initiative Competitive Grant 2011-68005-30411 from the USDA National Institute of Food and Agriculture and in part by the National Science Foundation under Grant Number EPS-1101284. The authors would like to thank Dr. Kurt Spokas and Dr. Rajesh Chintala for providing the field weathered biochars and Samuel Rathke for assistance in the laboratory. The authors are also grateful for reviewer comments which improved the quality of this manuscript.

References

[1] ASTM Standard D1762-84, Chemical Analysis of Wood Charcoal, ASTM International, West Conshohocken, PA, USA, 2007, http://dx.doi.org/10.1520/D1762-84R07

[2] R.B. Fidel, Biochar properties and impact on soil CO_2 and N_2O emissions, Dissertation. Iowa State University, 2015, http://lib.dr.iastate.edu/etd/14812/

[3] S. Archontoulis, I. Huber, F. Miguez, P. Thorburn, N. Rogovska, D. Laird, A model for mechanistic and system assessments of biochar effects on soils and crops and trade-offs, GCB Bioenergy (2016) doi:10.1111/gcbb.12314

[4] P. Blackwell, G. Riethmuller, M. Collins, Biochar application to soil, in: J. Lehmann, S. Joseph (Eds.), Biochar for Environmental Management: Science and Technology, Earthscans, London, 2009, pp. 207-226.

[5] C. Brewer, K. Schmidt-Rohr, J. Satrio, R. Brown, Characterization of biochar from fast pyrolysis and gasification systems. Environ. Prog. Sustain. Energy 28 (2009) 386-396. doi:10.1002/ep.10378

[6] A. Downie, A. Crosky, P. Munroe, Physical properties of biochar, in: J. Lehmann, S. Joseph (Eds.), Biochar for Environmental Management: Science and Technology, Earthscans, London, 2009, pp. 13-32.

[7] S. Bakshi, D. Aller, D. Laird, R. Chintala, Comparison of the physical and chemical properties of laboratory- and field-aged biochars, J. Environ. Qual. (2016) doi:10.2134/jeq2016.02.0062

[8] A. Mukherjee, A.R. Zimmerman, W.G. Harris, Surface chemistry variations among a series of laboratory-produced biochars, Geoderma 163 (2011) 247-255. doi:10.1016/j.geoderma.2011.04.021

[9] S. Hale. K. Hanley, J. Lehmann, A. Zimmerman, G. Cornelissen, Effects of chemical, biological, and physical aging as well as soil addition on the sorption of pyrene to activated carbon and biochar, Environ. Sci. Technol. 45 (2011) 10445-10453. doi: 10.1021/es202970x

[10] A. Cross, S. Sohi, A method for screening the relative long-term stability of biochar, GCB Bioenergy 5 (2013) 215–220. doi:10.1111/gcbb.12035

[11] A. Bradbury, F. Shafizadeh, Chemisorption of oxygen on cellulose char, Carbon 8 (1980) 109-116. doi:10.1016/0008-6223(80)90018-4

[12] P. Mitchell, T. Dalley, R. Helleur, Preliminary laboratory production and characterization of biochars from lignocellulosic municipal waste, J. Anal. Appl. Pyrol. 99 (2013) 71-78. doi:10.1016/j.jaap.2012.10.025

[13] A. Enders, K. Hanley, T. Whitman, S. Joseph, J. Lehmann, Characterization of biochars to evaluate recalcitrance and agronomic performance, Bioresour. Technol. 114 (2012) 644-653. doi:10.1016/j.biortech.2012.03.022

[14] X. Peng, L. Ye, C. Wang, H. Zhou, B. Suna, Temperature- and duration-dependent rice straw-derived biochar: Characteristics and its effects on soil properties of an Ultisol in southern China, Soil Till. Res. 112 (2011) 159-166. doi:10.1016/j.still.2011.01.002

[15] H.J. Bachmann, T.D. Bucheli, A. Dieguez-Alonso, D. Fabbri, H. Knicker, H.-P. Schmidt, A. Ulbricht, R. Becker, A. Buscaroli, D. Buerge, A. Cross, D. Dickinson, A. Enders, V.I. Esteves, M.W.H. Evangelou, G. Fellet, K. Friedrich, G. Gasco Guerrero, B. Glaser, U.M. Hanke, K. Hanley, I. Hilber, D. Kalderis, J. Leifeld, O. Masek, J. Mumme, M.P. Carmona, R. Calvelo Pereira, F. Rees, A.G. Rombolà, J.M. de la Rosa, R. Sakrabani, S. Sohi, G. Soja, M. Valagussa, F. Verheijen, F. Zehetner, Toward the standardization of biochar analysis: The COST action TD1107 interlaboratory comparison. J. Agric. Food Chem. 64 (2016) 513-527. doi:10.1021/acs.jafc.5b05055

[16] R. Calvelo Pereira, J. Kaal, M. Camps Arbestain, R. Pardo Lorenzo, W. Aitkenhead, M. Hedley, F. Macías, J. Hindmarsh, J.A. Maciá-Agulló, Contribution to characterization of biochar to estimate the labile fraction of carbon, Org. Geochem. 42 (2011) 1331-1342. doi.org/10.1016/j.orggeochem.2011.09.002

[17] O.R. Harvey, L.-J. Kuo, A.R. Zimmerman, P. Louchouarn, J.E. Amonette, B.E. Herbert, An index-based approach to assessing recalcitrance and soil carbon sequestration potential of engineered black carbons (biochars), Environ. Sci. Technol. 46 (2012) 1415-1421. doi:10.1021/es2040398

[18] T. Wang, M. Camps-Arbestain, M. Hedley, Predicting C aromaticity of biochars based on their elemental composition. Org. Geochem. 62 (2013) 1-6. doi.org/10.1016/j.orggeochem.2013.06.012

[19] F. Ronsse, S. Van Hecke, D. Dickinson, W. Prins, Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions, GCB Bioenergy, 5 (2013) 104-115. doi:10.1111/gcbb.12018

[20] T. Wang, M. Camps-Arbestain, M. Hedley, B.P. Singh, R. Calvelo-Pereira, C. Wang, Determination of carbonate-C in biochars, Soil Research 52 (2014) 495-504. doi.org/10.1071/SR13177

[21] A. Budai, A. Zimmerman, A. Cowie, J. Webber, B. Singh, B. Glaser, C. Masiello, D. Andersson, F. Shields, J. Lehmann, M. Camps-Arbestain, M. Williams, S. Sohi, S. Joseph, Biochar carbon stability test method: an assessment of methods to determine biochar carbon stability. International Biochar Initiative. (2013) http://www.biocharinternational.org/sites/default/files/IBI_Report_Biochar_Stability_Test_Method_Final.pdf

[22] K. Spokas, Review of the stability of biochar in soils: predictability of O:C molar ratios, Carbon Manag. 1 (2010) 289-303. doi:10.4155/cmt.10.32

Appendix - supplementary data

Table S1. Details of biochars used in this study (adapted from Bakshi et al., 2016). Six un-weathered (Fresh-1), 6 laboratory-weathered (LW), 5 un-weathered but stored (Fresh-2), and 5 field-weathered (FW) biochars were investigated.

Biochar name	Pyrolysis technique	Biomass feedstock	Pyrolysis temperature (°C)	Mode of weathering	Source
HS1	Slow	Hardwood	600-650	Fresh-1, LW	Royal Oak Charcoal, USA
HS2	Slow	Hardwood	500-550	Fresh-2, FW	Cowboy Charcoal, Brentwood, TN, USA
SS	Slow	Switchgrass	500	Fresh-1, LW	Iowa State University, Ames, IA, USA
CS	Slow	Corn stover	500	Fresh-1, LW	Iowa State University, Ames, IA, USA
HF	Fast	Hardwood	500-550	Fresh-1, LW	Dynamotive Energy Systems, Richmond, Canada
SF	Fast	Soybean	500	Fresh-1, LW	BioCentury Research Farm, Boone, IA, USA
CF	Fast	Corn stover	500	Fresh-1, LW	Avello Bioenergy, Boone, IA, USA
MNS	Fast	Macadamia Nut Shell	500-550	Fresh-2, FW	Biochar Brokers, Denver, CO, USA
HG	Gasification	Hardwood	800-850	Fresh-2, FW	Biochar Solutions, Inc, Carbondale, CO, USA
SG	Gasification	Switchgrass	800-850	Fresh-2, FW	Biochar Solutions, Inc, Carbondale, CO, USA
CG	Gasification	Corn stover	800-850	Fresh-2, FW	Biochar Solutions, Inc, Carbondale, CO, USA

Table S2. Moisture content values for the Fresh-1 biochars as determined by the ASTM method and modified method. Data is the average of three replicates ± one standard error of the mean.

Biochar name	ASTM method	Modified method
Fresh-1 HF	2.947 (±0.083)	4.004 (±0.137)
Fresh-1 HS1	2.004 (±0.062)	4.238 (±0.108)
Fresh-1 SF	0.388 (±0.069)	2.581 (±0.502)
Fresh-1 SS	-0.213 (±0.033)	3.042 (±0.337)
Fresh-1 CF	1.932 (±0.060)	3.183 (±0.397)
Fresh-1 CS	-0.042 (±0.169)	4.062 (±0.131)

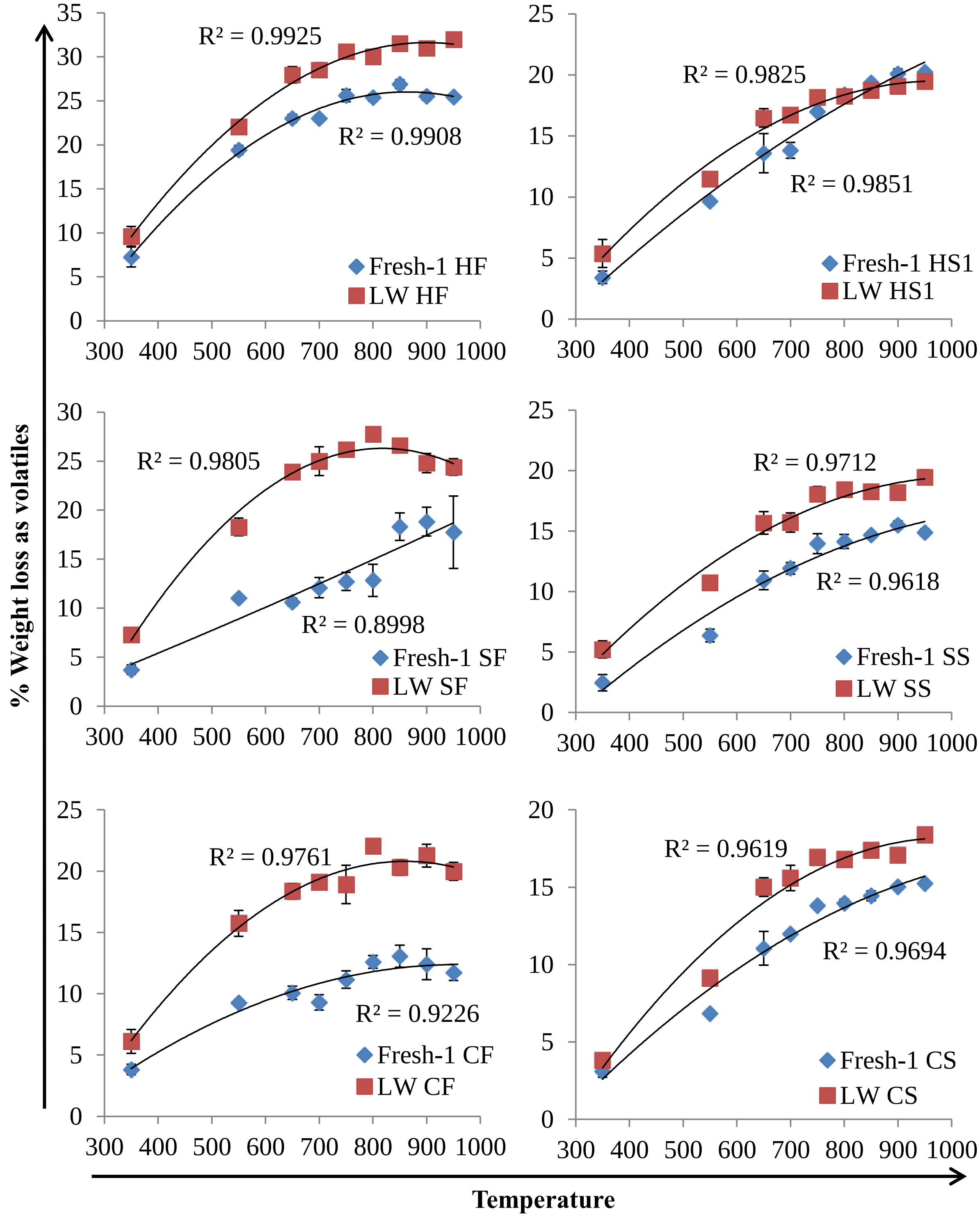
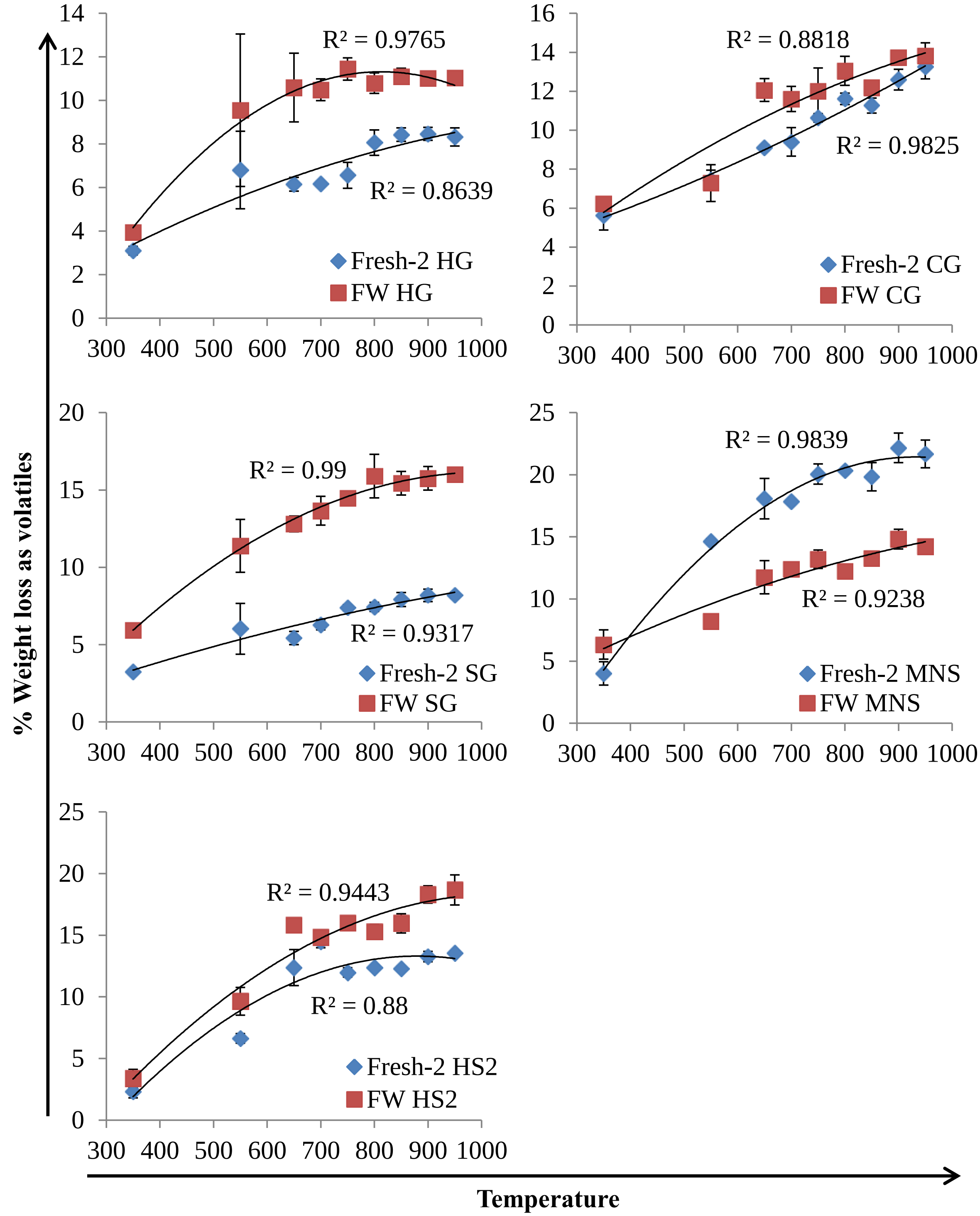


Fig. S1. Relationship between % weight loss as volatiles and temperature for fresh (Fresh-1 and Fresh-2) and weathered (FW and LW) biochars produced by fast pyrolysis, slow pyrolysis, or gasification. All biochars were analyzed at nine different temperatures to separate VM from FC. Error bars indicate standard error of three replicates.



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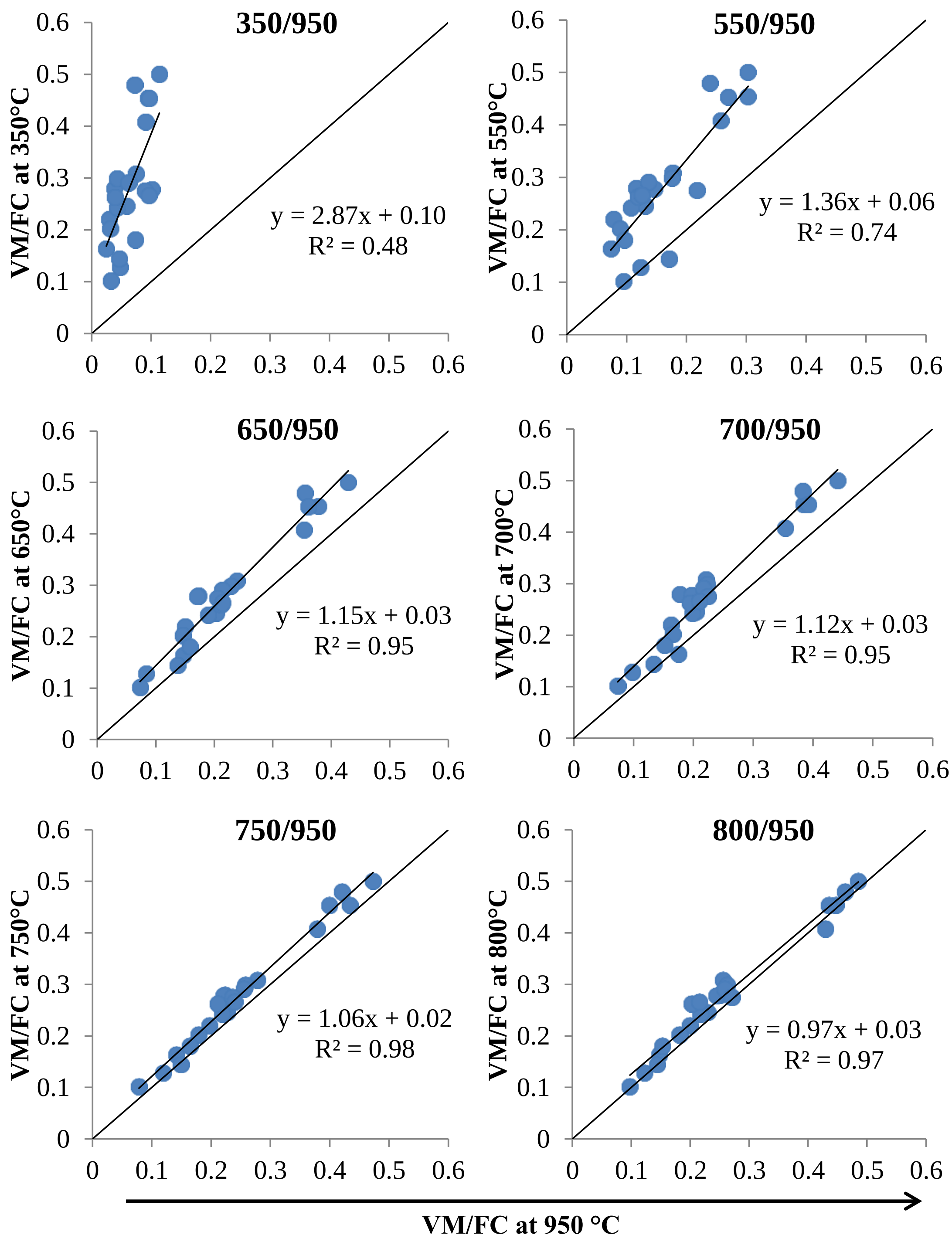
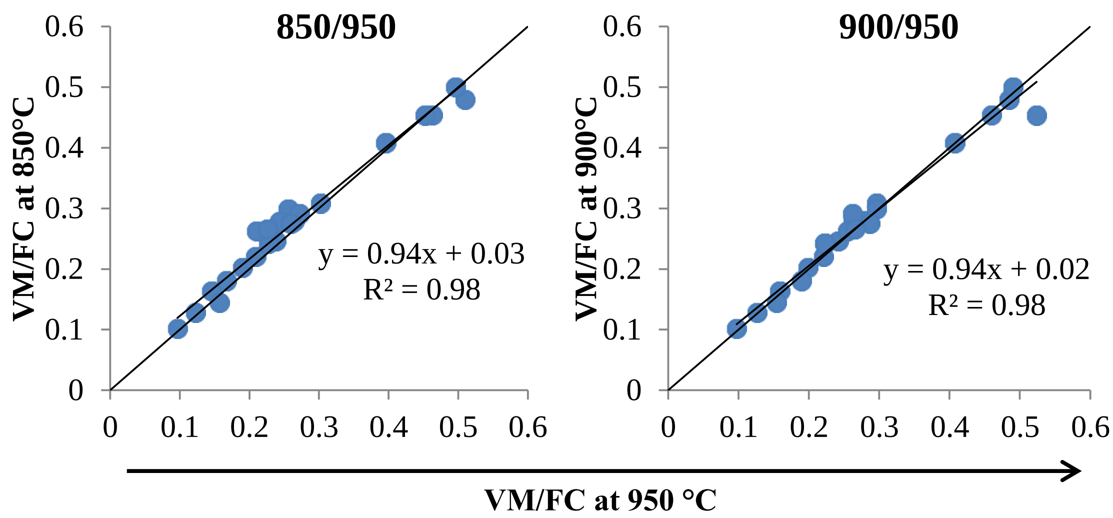


Fig. S2. Comparison of apparent VM/FC ratios determined using VM and FC separation temperatures ranging from 350 °C to 900 °C (y-axis) with VM/FC ratios determined at 950 °C (x-axis).



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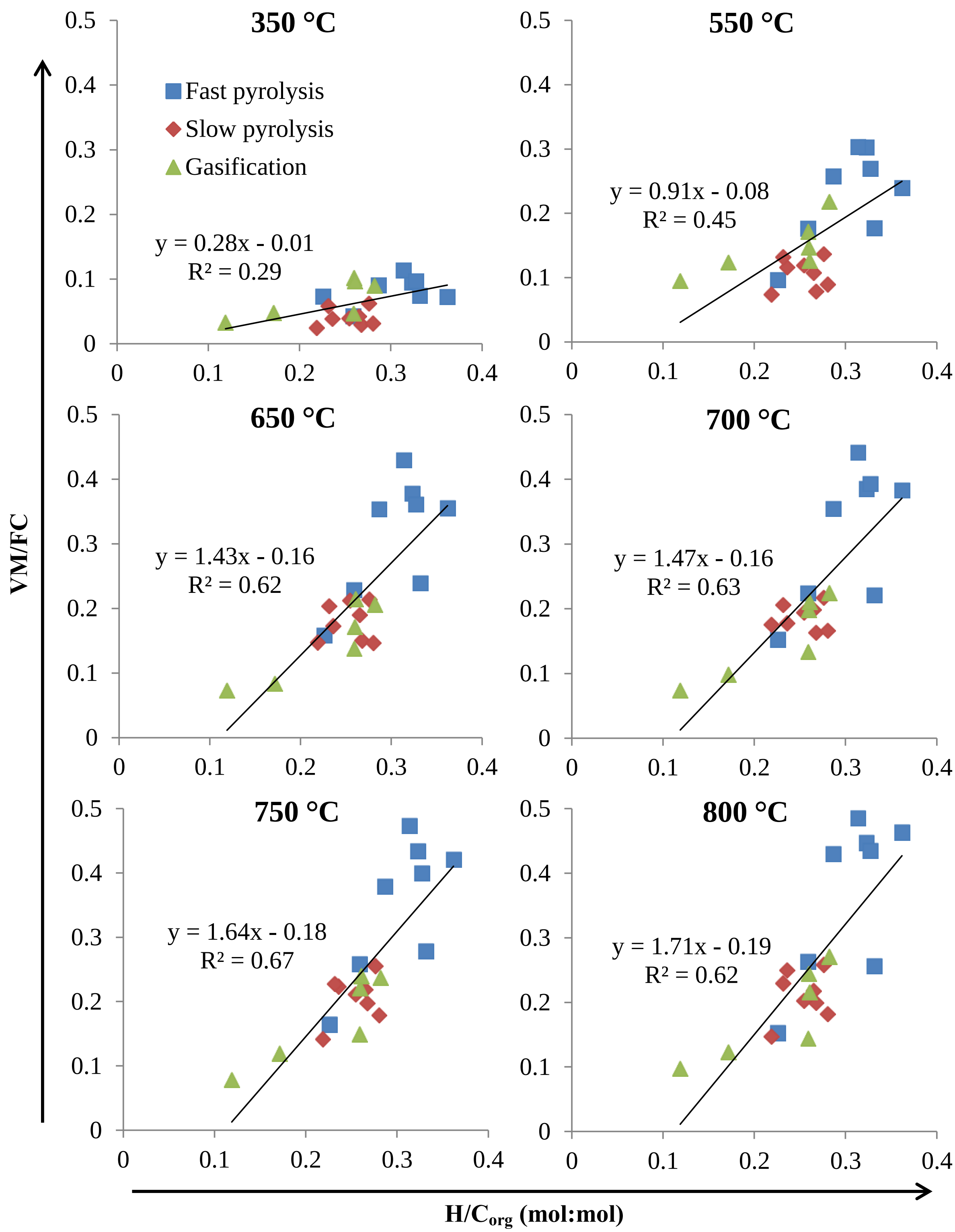

Fig. S3. VM/FC vs. H/C_{org} (mol:mol) ratio as determined from 350- 950 °C for all biochars grouped by production technique. VM and FC are on a dry ash free basis.

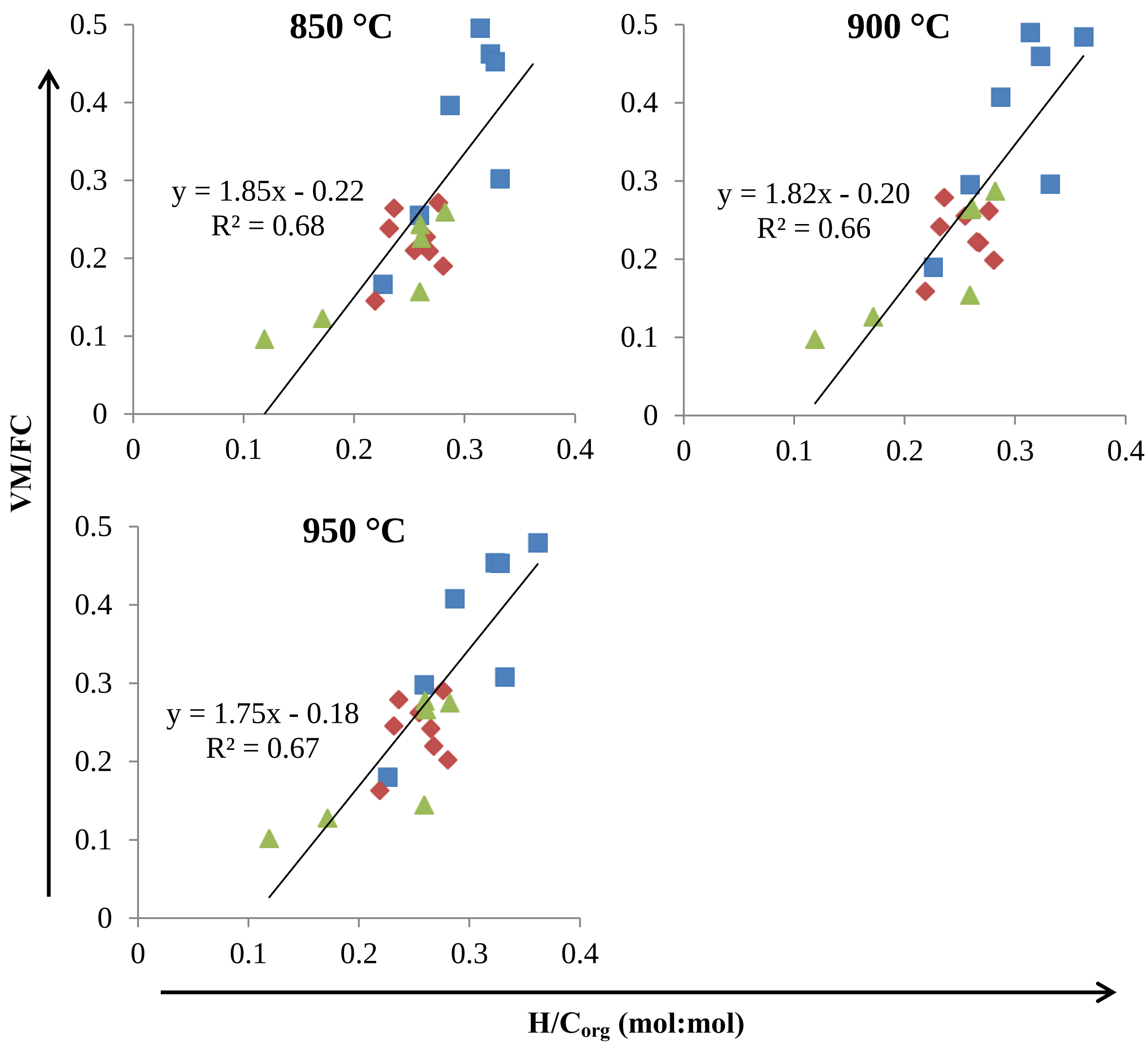

Fig. S3. Continued

CHAPTER 3. BIOCHAR AGE AND CROP ROTATION IMPACTS ON SOIL QUALITY

Modified from a manuscript published in Soil Science Society of America Journal

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Abstract

Corn residue removed from Midwestern farms is a large potential source of biomass for cellulosic bioenergy production in the US long-term harvesting of biomass, however, may lead to the degradation of soil quality unless management practices that compensate for the removal of biomass are used. In this study, biochar amendments and long-term crop rotations that include triticale and switchgrass with corn and soybeans were hypothesized to reduce the negative effects of biomass harvesting on soil quality. Chemical breakthrough curves, measured for intact soil cores indicate that crop rotations that include switchgrass or triticale increased both retardation and dispersivity relative to conventional rotations and biochar amendments decreased dispersivity relative to controls. Across all crop rotations, there was an increase in total soil C and N, soil C/N ratio, pH and gravity drained water content, and a decrease in bulk density for soils treated with biochar relative to no-biochar controls. No significant effect of biochar age on soil physical properties was measured in 2014 but significant increases with biochar age were found for total soil C and N in 2016, suggesting a synergistic interaction (negative priming). Continuous switchgrass stands were found to build soil organic C and N, increase retention of plant available P and K, and lower bulk density relative to the continuous corn cropping system.

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The results suggested that soil biochar amendments and crop rotations that included switchgrass helped mitigate some of the adverse effects of biomass harvesting on soil quality.

Abbreviations: BC, biochar; CDE, convection-dispersion equation; EC, electrical conductivity; K_s, saturated hydraulic conductivity; LTRPs, long-term rotation plots; R, retardation; λ, dispersivity.

Core Ideas

- Crop rotations including switchgrass were found to build soil organic C and N
- Biochar amendments increased soil C and N, pH, and gravity drained water content
- Total soil C and N increases with biochar age, suggests negative priming
- Biochar and switchgrass offset negative effects of biomass harvesting on soil quality

Introduction

Energy produced from biomass has been proposed as a means of simultaneously improving domestic energy security, reducing greenhouse gas emissions, and revitalizing rural economies. Specifically, corn crop residue harvested from Midwestern farms was identified as the largest available source of biomass for bioenergy production (Perlack et al., 2005; Perlack and Jones, 2011; Langholtz et al., 2016). However, corn crop residues are typically returned to the soil as a conservation practice to increase soil organic matter levels, reduce erosion by wind and water, enhance biological activity, and maintain overall soil quality (Collins et al., 1992; Wilhelm et al., 2004; Blanco-Canqui, 2010). Significant concerns have arisen over the long-term sustainability of biomass harvesting as rates of biomass removal have increased and are likely to continue to increase along with the growing bioenergy industry.

The effects of residue removal on agricultural productivity and environmental quality are site specific and time dependent, with some studies indicating that the removal of aboveground biomass negatively affects crop yield and soil and water quality (Mann et al., 2002; Cruse and Herndl, 2009; Blanco-Canqui and Lal, 2009). However, evidence from the upper Midwest suggests that the removal of aboveground biomass leads to no change or an increase in corn yields in the short-term (Kaspar et al., 1990; Karlen et al., 2011; Rogovska et al., 2016), while reducing soil and water quality in the long-term. For example, it was found that after 19 yr of residue removal on corn and soybean plots in southern Minnesota, the effective cation exchange capacity, N mineralization potential, and soil organic carbon levels decreased by 7.3, 28, and 12%, respectively (Laird and Chang., 2013).

Crop residues impact soil nutrient cycling as they contain important plant nutrients such as N, P, S, K^+, Ca^{2+}, and Mg^{2+}. When residues are not returned to the field, soil fertility is reduced and a farmer's reliance on synthetic fertilizers increases (Lal, 2008). Crop residues also contribute to the maintenance of soil organic matter levels, which has a large impact on soil biological, chemical, and physical properties by providing energy for microbes, buffering soil pH, and increasing soil water retention (Wilhelm et al., 2010). Studies show that when residue removal rates increase the labile C fractions and potentially mineralizable C and N pools decrease (Halpern et al., 2010), similarly particulate organic matter and total soil C and N levels decrease (Hammerbeck et al., 2012). Furthermore, soil physical properties are affected by residue removal; for example soil aggregate stability decreases with increasing residue removal (Stetson et al., 2012). The degradation of soil structure has implications for soil water retention, bulk density, and aeration (Carter, 2002). To avoid the possible long-term negative impacts of biomass harvesting on soil quality new cropping systems are needed that support sustainable residue harvesting for bioenergy production while simultaneously protecting soil resources from erosion, sequestering soil carbon, and building soil quality.

Crop rotations, the practice of growing a sequence of crop species for successive years on the same land, are an important agricultural management strategy for enhancing soil fertility and productivity (Yates, 1954; Bullock, 1992; Karlen et al., 1994). Previous studies have shown that including perennial grasses and/or legumes in crop rotations, improves soil structure (Kay, 1990; Robinson et al., 1994), increases soil organic carbon levels (Russell et al., 2005; Blanco-Canqui, 2013), and reduces soil erosion (Liebman et al., 2013). Rotations have also been shown to increase soil microbial activity, which influences nutrient cycling, soil aggregation, and carbon sequestration (Giller et al., 1997). A study by Russell et al. (2006) found that the inclusion of alfalfa in crop rotations increased N availability and potential N mineralization rates relative to continuous corn receiving 180 kg N ha^{-1}. Similarly, crop rotations that included a 3-yr forage decreased soil bulk density, increased total organic C, and improved soil aggregation (Karlen et al., 2006).

Historically, both short- and long-term crop rotations were commonplace even on the highly fertile soils of the US corn-belt region (Karlen et al., 1994). Today, long-term crop rotations on the Midwestern landscape are uncommon. Crop rotations, due to their spatial and temporal diversity, contribute to improving soil and environmental quality, as well as a wide range of ecosystem services (Asbjornsen et al., 2013; Lal, 2015). A study by Davis et al. (2012) found that cropping systems that support more diverse rotations can reduce fertilizer and pesticide requirements while maintaining similar yield and economic profitability compared to less diverse systems. Rotations have also been found to increase nutrient and water retention, due mostly to increased pore space and root biomass (Karlen et al., 1994). Furthermore, diverse crop rotations reduce disease outbreaks and disrupt pest cycles by interrupting carry-over effects between crops (Dabbert and Madden, 1986; Edwards, 1989; Tilman et al., 2002).

Biochar, the solid co-product of the thermochemical conversion of biomass to bioenergy, is another means to improve soil quality, enhance ecosystem sustainability, and improve agricultural productivity. The potential positive impacts of biochar on soil quality and as a long term carbon sequestration agent were emphasized nearly a decade ago (Laird, 2008). The effects of biochar amendments on soil properties are variable, and are influenced by biochar feedstock and production conditions, as well as soil type and climate. In general, however, biochars have high porosity, high surface area, and both polar and non-polar surface chemistry which influences soil water and nutrient retention. In a soil column experiment, biochar led to decreased nutrient leaching (Laird et al., 2010a), while in a field study biochar increased available soil water content (Rogovska et al., 2014). Biochar has also been reported to have indirect effects on soil physical properties by altering aggregation, bulk density, hydraulic conductivity, and soil micro- and macro-porosity (Bot and Benites, 2005; Gaskin et al., 2007; Thies and Rilling, 2009; Hardie et al., 2014). Due to the chemical properties of biochar, studies show increases in soil pH, cation exchange capacity, anion exchange capacity, and total soil C and N following biochar applications (Rondon et al., 2006; Lawrinenko and Laird, 2015; Mukherjee and Lal, 2016). Biochar also increases soil microbial activity (Steiner et al., 2008; Lehmann et al., 2011), however, the mechanisms by which this occurs are still largely unknown (Thies et al., 2015).

The degree of biochar weathering or aging alters the influence of biochar on soil properties. Increased exposure to physical, chemical, and biological processes in the soil, changes biochar properties (Downie et al., 2009). For example, biochars tend to become more hydrophilic with time as the number of oxygen- containing functional groups on biochar surfaces increases. This change in the surface chemistry of biochar over time can for example, influence the sorption of organic compounds (Qian and Chen, 2014). The effect of biochar age on soil properties is critical and an area needing further research (Mukherjee and Lal, 2016). Changes in the physical and chemical properties of biochar have been investigated in several laboratory weathering studies (Hale et al., 2011; Mukherjee and Lal, 2013; Bakshi et al., 2016), however, few studies have addressed changes in soil properties as a function of biochar age following the addition of biochar to soil in a field study. Major et al. (2010) evaluated the effect of biochar that had been in the soil for 3 and 4 yr on soil hydrology and nutrient leaching in a savanna Oxisol. Another study investigated the effect of biochar and manure on water vapor sorption in a sandy loam soil after biochar was applied at various rates and in two different years (Arthur et al., 2015).

To the best of our knowledge, no prior studies have evaluated biochar impacts on soil properties as a temporal series of biochar age or the interaction effects of biochar and cropping rotations on selected soil quality indicators. The goal of this study was to investigate the effects of biochar, biochar age, and cropping rotations, as well as their interactions, on a series of soil physical and chemical properties. We hypothesized that biochar amendments and crop rotations that include small grains and perennial grasses will enhance soil quality, and hence, the sustainability of bioenergy cropping systems. We also hypothesized that the degree of biochar aging will impact measured soil quality parameters. Lastly, we hypothesized that there will be a synergistic interaction between biochar and crop rotations on soil quality.

Material and Methods

Study Site and Sample Collection

The soil samples used in this study were collected from long-term rotation plots (LTRPs), which were established in central Iowa in 2006 to investigate the sustainability of diverse bioenergy cropping systems. The LTRPs are located on the Sorenson Research Farm, part of the Iowa State University Agronomy and Agricultural Engineering Research Farms in Boone County, IA. The dominant soil series at the site are Webster (Fine-loamy, mixed, superactive, mesic Typic Endoaquoll), Clarion (Fine-loamy, mixed, superactive, mesic Typic Hapludoll), and less than 1% of Nicollet (Fine-loamy, mixed, superactive, mesic Aquic Hapludoll). The study site is comprised of 112 whole plots. Sixteen of the whole plots are in continuous switchgrass, and these are not split into subplots. The other 96 whole plots are split into 192 subplots, with biochar applied on one-half of each split plot. Hence, we have 16 continuous switchgrass whole plots plus 4 crop rotations x 6 phases of each rotation x 2 biochar subplot treatments x 4 replications for a total number of 208 plots. Whole plot dimensions are 9.1 m by 9.1 m with subplots having dimensions of 4.6 m by 9.1 m.

The study included five different crop rotations: continuous corn (Rot. 1), alternating corn–soybean (Rot. 2), corn–soybean–triticale/soybean–corn–soybean–triticale/soybean (Rot. 3), corn–corn–corn/switchgrass–switchgrass–switchgrass–switchgrass (Rot. 4), and continuous switchgrass (Rot. 5). Rotations were in a 6-yr cycle with all phases of each rotation present every year in four replicate blocks. Since establishment, residue management at the site has been 100%

removal of aboveground biomass from all plots containing corn, switchgrass, and triticale. The small grain triticale (*Triticosecale* ‘Pronghorn’), a high-yielding interspecific hybrid of wheat and rye, was selected because it is well adapted to the climatic and environmental conditions of Iowa and serves as a biomass crop. Switchgrass (*Panicum virgatum* ‘Cave-in-Rock’) was included because it is a well-established herbaceous biomass crop for bioenergy and its extensive root system has been shown to increase soil carbon, reduce soil erosion, and improve overall soil health (Heaton et al., 2008).

In 2012 after one complete rotation cycle (6 yr), all plots, except Rot. 5, were split into subplots. Prior to planting the biochar was incorporated at a rate of 22.4 t ha-1 with a single pass of a rotary tiller to a depth of 20 cm. Biochar applications were at the subplot level over a 4-yr period to achieve application to all subplots that followed the corn phase of each rotation. In spring 2012, the first 36 subplots received biochar, in spring 2013, 36 more subplots received biochar, in spring 2014, 20 more subplots received biochar and lastly in spring 2015, 4 more subplots had biochar incorporated. Biochar was applied at the same rate and by the same technique in each of the 4 yr. The biochar applied was the Royal Oak Enterprises #10 granular charcoal. This is a slow pyrolysis (600–650°C) biochar produced from hardwood. Physical and chemical properties of the biochar are provided in Table 1. Prior to 2015 all plots and subplots were under strict no-till management with the exception of a one-time roto tillage operation to incorporate biochar into the subplots that received biochar. To equalize the tillage effect, all plots, with the exception of plots that contained switchgrass in Rot. 4 and 5, were tilled with a single pass of a rotary tiller to a depth of 20 cm in the spring of 2015 before planting.

The first set of soil samples was collected from 96 of the 112 whole plots in spring 2006 at the time of study establishment to obtain baseline soils information (sampling did not include the switchgrass plots). A second set of soil samples was collected from all 208 plots in spring 2014. At this time, a total of 72 subplots contained biochar, with 36 of these subplots having biochar field aged for 2 yr and 36 subplots had biochar field aged for 1 yr. Undisturbed surface soil cores, 0 to 10 cm depth, were collected using a hydraulic probe mounted on the back of a tractor, from all 208 plots prior to planting and biochar application. The top 2.4 cm of every core was discarded to minimize the effects of tillage. This resulted in all cores with a final height of 7.6 cm and diameter of 7.6 cm. The intact soil cores were wrapped in plastic, bagged in the field, and refrigerated for later analysis. The third set of soil sampling from all 208 plots again took place in spring 2016. At the time of the 2016 sampling, a total of 96 subplots contained biochar; 36 subplots had biochar aged 4 yr, 36 subplots had biochar aged 3 yr, 20 subplots had biochar aged 2 yr, and 4 subplots had biochar aged 1 yr. Soil cores were collected from all plots in the same way as described for the 2014 sampling.

Table 1. General properties of the hardwood Royal Oak #10 granular biochar applied at the study site. All values are averages of three replicates with standard error.

Property[†]	**Value**
pH (1:15 H_2O)	7.0 (0.02)
EC, µS cm^{-1}	212 (0.8)
% C	76.6 (0.43)
% H	2.7 (0.01)
% N	0.38 (0.001)
C:N	232 (2.0)
$H:C_{org}$	0.21 (0.001)
SSA, m^2 g^{-1}	194 (0.7)- EGME method 87 (2.6)- BET-N_2 method
CEC, $cmol_c$ kg^{-1}	3.2 (0.3)
AEC, $cmol_c$ kg^{-1}	2.5 (0.12)
% Volatile matter	17 (0.2)

Table 1. Continued

% Fixed carbon	71.5 (3.5)
% Ash	7.02 (0.09)

† EC: electrical conductivity, SSA: specific surface area, EGME: Ethylene glycol monoethyl ether, BET: Brunauer, Emmett and Teller, CEC: cation exchange capacity, AEC: anion exchange capacity.

Laboratory Analyses

Saturated hydraulic conductivity (K_s), a saturated steady-fluid-flow displacement experiment (transport experiment), and gravity drained soil water content measurements were performed on the intact cores collected in 2014. In preparation for the analyses, the bottom of each intact core was covered with four layers of cheesecloth and an empty cylinder with the same dimensions as the soil core was taped to the top end of the intact core. Prepared cores were placed into a vacuum chamber and saturated with 0.001M $CaCl_2$ (resident solution) overnight (≥ 12 hours). Complete saturation was assumed to be achieved once all cores had visible ponding of solution on the surface. Saturated soil cores were mounted on a ring stand, and a 5 cm head of the 0.001M $CaCl_2$ resident solution was applied and maintained using a Mariotte bottle. Once solution flow through a soil core reached steady state, K_s was determined by the constant head method (Klute and Dirksen, 1986). K_s (m s^{-1}) was estimated with the following form of Darcy's equation:

$$K_s = \left(\frac{Q}{At}\right)\left(\frac{L}{H}\right)$$

where Q is the total volume of outflow (m^3) in a time period, t (s), A is the cross-sectional area of the soil core (m^2), L is the length of the soil core (m), and H is the hydraulic head (m). The hydraulic head is equal to the length of the soil core plus the depth of solution ponded on the soil surface. The outflow rate was measured using a graduated cylinder and stopwatch. Reported outflow rates are averages of five outflow measurements for each soil core.

Following the collection of K_s data, a transport experiment was conducted with the aid of a fraction collector. The flow of resident solution through a soil core was stopped after the head decreased to the soil surface, at which time a tracer solution (0.005M $CaCl_2$) head was initiated and flow of the tracer solution began. While the tracer solution was flowing, effluent was simultaneously collected from the bottom of the core. Forty sequential test tube fractions of effluent, based on the time interval used for the determination of K_s, were collected for each core. Mass (g) and EC (μS cm^{-1}) of the effluent in each test tube was measured (FE30, Five Easy Conductivity Meter, Mettler Toledo, Switzerland). The measured chemical breakthrough curves for each soil core were modeled using the convection-dispersion equation (CDE) at equilibrium within the CXTFIT solver function in Excel (Parker and van Genuchten, 1984; Tang et al., 2010). The CDE function describes solute transport as:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z}$$

where R is the dimensionless retardation factor, C is the solution concentration (M L^{-1}), t is time (s), z is the distance from the inlet (cm), D is the dispersion coefficient which is assumed to equal λ*v, where λ is dispersivity (cm), and v is the average pore-water velocity (cm s^{-1}). Average pore-water velocity is determined by the two measured parameters of flux and volumetric water content (Skaggs et al., 2002). For model fitting, user inputs were supplied for initial and boundary conditions, fixed parameters of velocity and column length as well as the concentration per pore volume data. Least squares fits of the model to the data provided values of R and λ for each soil core. The CXTFIT program also provided statistical parameters including residuals, standard deviations, sums of squares, R^2, and upper and low confidence limits based on the student *t* distribution.

At the completion of the tracer experiment soil cores were allowed to freely drain to equilibrate before being weighed. The oven-dry weight of soil in the cores was determined by weighing after the soil had been oven-dried at 105°C overnight. Gravity drained water content (g g^{-1}) and bulk density (g cm^{-3}) were determined by dividing the weight of water retained by the oven-dry weight and the oven-dry weight by the core volume for each core, respectively. Gravimetric water content was converted to volumetric water content (cm^3 cm^{-3}) using the density of water and the measured bulk density for each core. The data presented for volumetric water content is only for the soil cores collected in 2014, while the bulk density data is presented for soil cores collected in both 2014 and 2016 (Table 2).

The 208 soil samples collected in spring 2016 were analyzed for various chemical properties: pH, EC, total C, total N, and Mehlich III extractable phosphorous (P) and potassium (K). Soil samples were passed through a 2.0 mm sieve and air-dried. Soil pH and EC (1:10 soil-distilled water) were measured using a pH/conductivity meter (M 545P, Pinnacle Series, Nova Analytics Corp., CA). Total C and total N were determined using a C/N combustion analyzer (Vario Microcube, Elementar Analysensysteme GmbH, Germany). Plant available soil P and K concentrations were determined using the Mehlich III extraction method and analyzed by inductively coupled plasma-atomic emission spectroscopy (Mehlich, 1984). Bulk density (g cm^{-3}) was determined after oven drying at 105°C the sieved samples and dividing the oven-dry sample weight by the known volume of the soil cores.

Table 2. Physical and chemical properties measured in 2014. Values are the average of four replicates with standard error and are grouped by crop rotation and biochar. Only no biochar plots were used in comparing crop rotations. Biochar effect (yes, no) does not include Rot. 5 data. Different letters indicate significance between factors within a group ($P < 0.05$).

Property†	**Crop rotation**					**Biochar treatment**‡	
	Rot 1	**Rot 2**	**Rot 3**	**Rot 4**	**Rot 5**	**Yes**	**No**
Log K_s, cm d^{-1}	0.221**b** (0.156)	0.770**ab** (0.266)	1.096**a** (0.196)	1.229**a** (0.221)	0.881**ab** (0.315)	0.894**a** (0.123)	0.829**a** (0.110)
R	0.963**b** (0.045)	1.137**ab** (0.178)	1.135**ab** (0.080)	1.546**a** (0.206)	1.214**ab** (0.267)	1.034**a** (0.038)	1.194**a** (0.071)
λ, cm	6.118**b** (0.800)	13.617**ab** (6.509)	11.278**ab** (2.966)	25.134**a** (6.131)	6.602**b** (1.026)	7.609**a** (1.963)	13.804**a** (2.283)
VWC, cm^3 cm^{-3}	0.412**a** (0.004)	0.416**a** (0.007)	0.413**a** (0.005)	0.402**a** (0.006)	0.417**a** (0.009)	0.445**a** (0.004)	0.410**b** (0.003)
BD, g cm^{-3}	1.511**a** (0.011)	1.479**ab** (0.020)	1.482**ab** (0.015)	1.512**a** (0.010)	1.430**b** (0.027)	----	----

† K_s, saturated hydraulic conductivity; R, retardation; λ, dispersivity; VWC, volumetric water content; BD, bulk density; Rot 1, continuous corn; Rot 2, alternating corn-soybean; Rot 3, corn-soybean-triticale/soybean-corn-soybean-triticale/soybean; Rot 4, corn-corn-corn/switchgrass-switchgrass-switchgrass-switchgrass; Rot 5, continuous switchgrass.
‡Combined effects of biochar and tillage, which are confounded in the 2014 data set.

Statistical Analyses

The LTRPs experimental design is a randomized complete block design with a split-plot (i.e., subplots) arrangement of treatments in four replicate blocks. Main plots consisted of five cropping rotations and were divided into subplots to distinguish the biochar and no biochar treatments except for the continuous switchgrass rotation (Rot.5) which never received biochar. Biochar age (0, 1, 2, 3, and 4 yr) was considered at the subplot level. The data were analyzed using the MIXED procedure (SAS Institute, 2013) to determine the effects of cropping rotation, biochar presence and/or absence, biochar age, and their interactions on measured soil physical and chemical properties. The MIXED model was used to accommodate unbalanced or missing data in the analysis and to account for all random and fixed effects. Year and block were considered as random effects, while fixed effects included biochar, biochar age, and rotation. The effect of biochar and the interaction effect of biochar*rotation were evaluated excluding Rot. 5, as biochar was never incorporated in that rotation. Differences between crop rotations were determined using only no biochar data to allow a valid comparison with Rot. 5. Treatments means were compared using a *t* test. Statistical significance was assessed at the 5% α level and all reported data are means of four true field replicates.

Results and Discussion

Saturated hydraulic conductivity varied widely across samples analyzed. The slowest K_s value was 0.03 cm d^{-1}, the fastest was 7582 cm d^{-1}, and the average across all soil cores was 192 cm d^{-1}. Because of this wide range and non-normal distribution of K_s values, the K_s data were log-transformed. After log-transformation, three outliers, as evidenced by values greater than one standard deviation from the mean, were removed from the dataset. Statistical analysis was done using the normally distributed log-transformed K_s dataset (Table 2).

Saturated hydraulic conductivity was found to be significantly lower in Rot. 1 compared to rotations 3 and 4. No other significant differences were found among crop rotations and biochar treatments (Table 2) or biochar age (data not shown). Our finding that biochar did not affect K_s was consistent with several previous studies (Laird et al., 2010b; Jeffery et al., 2015) and inconsistent with others (Uzoma et al 2011; Lim et al., 2016). A possible reason for the lower K_s under continuous corn (Rot. 1) compared to rotations that included triticale (Rot. 3) and switchgrass (Rot. 4) was greater soil compaction and less pore continuity in the soils under continuous corn, however, this did not explain why Rot. 5 (continuous switchgrass) did not differ from Rot. 1. The large amount of root biomass found under perennial grass stands, and hence, the potential blocking of soil pores, however, could explain the lower K_s observed in Rot. 5. Changes in saturated hydraulic conductivity due to the presence of plant roots have been reported previously (Morgan et al., 1995; Ola et al., 2015). Overall, the presence of outliers and much of the variability in K_s was attributed to preferential flow resulting from earthworm holes and other continuous macropores, which allowed water to freely drain through the cores. Increased earthworm density and higher infiltration rates have been observed in more diverse crop rotations compared to continuous corn and corn-soybean rotations (Katsvairo et al., 2002). This provided another possible explanation for the higher K_s values observed for Rot. 3 and 4, which included triticale and switchgrass, respectively.

Following the determination of K_s, a transport experiment using a $CaCl_2$ tracer was conducted to determine chemical breakthrough curves and the solute transport property known as dispersivity, λ. Dispersivity is related to soil structure, which may change over time as biochar weathers in soil under field conditions. Our results indicate no overall effect of crop rotation or biochar on chemical transport through the soil columns (Fig. 1) but a significant biochar rotation interaction, as R and λ decreased due to biochar in Rot. 4 (P = 0.02) and (P = 0.0068), respectively (Table 2). Further, biochar and biochar age had no effect on R and λ, and a significant year effect was found for the impacts of λ (data not shown).

Particle density was assumed to be 2.65 g cm^{-3} for all soil cores. This value was used to calculate porosity and hence relative pore volume in the solute transport experiment. However, biochars usually have a lower particle density than other soil solids, typically 1.5 to 1.7 g cm^{-3}, but it can be as high as 2.25 g cm^{-3} (solid graphite) (Brewer, 2012). Thus, the addition of biochar lowers the average particle density of a soil and consequently may result in an overestimation of porosity for the soil cores containing biochar. In effect, the solute concentration, for a given pore volume, moving through the soil cores that contain biochar may be underestimated. However, this had a minimal impact on overall results of the solute transport experiment because of the low rate of biochar application in the field (22.4 t ha^{-1}).

Soil moisture retention is an important indicator of soil quality and is often key to improving crop productivity. Here we measured gravity-drained water content after soil cores had freely drained for 24 h. No biochar rotation interaction effect or individual effect of rotation (Table 2) and biochar age (data not shown) was found on gravity drained volumetric water content (cm^3 cm^{-3}). However, the biochar treatments significantly ($P < 0.0001$) increased gravity drained volumetric water content values (Fig. 2). This was expected since biochar has a direct influence on soil water storage as a result of its high internal porosity, high surface area, and relatively polar surface chemistry. This result is in agreement with some previous studies (Glaser et al., 2002; Novak et al., 2009; Streubel et al., 2011; Artiola et al., 2012; Basso et. al., 2013) but not all (Major et al., 2012; Jeffery et al., 2015). The ability of biochar additions to increase soil water retention has the potential under certain conditions to positively impact crop yields (Verheijen et al., 2010). This is especially true when the capacity of the soil to retain water limits crop productivity (Bruun et al., 2014).

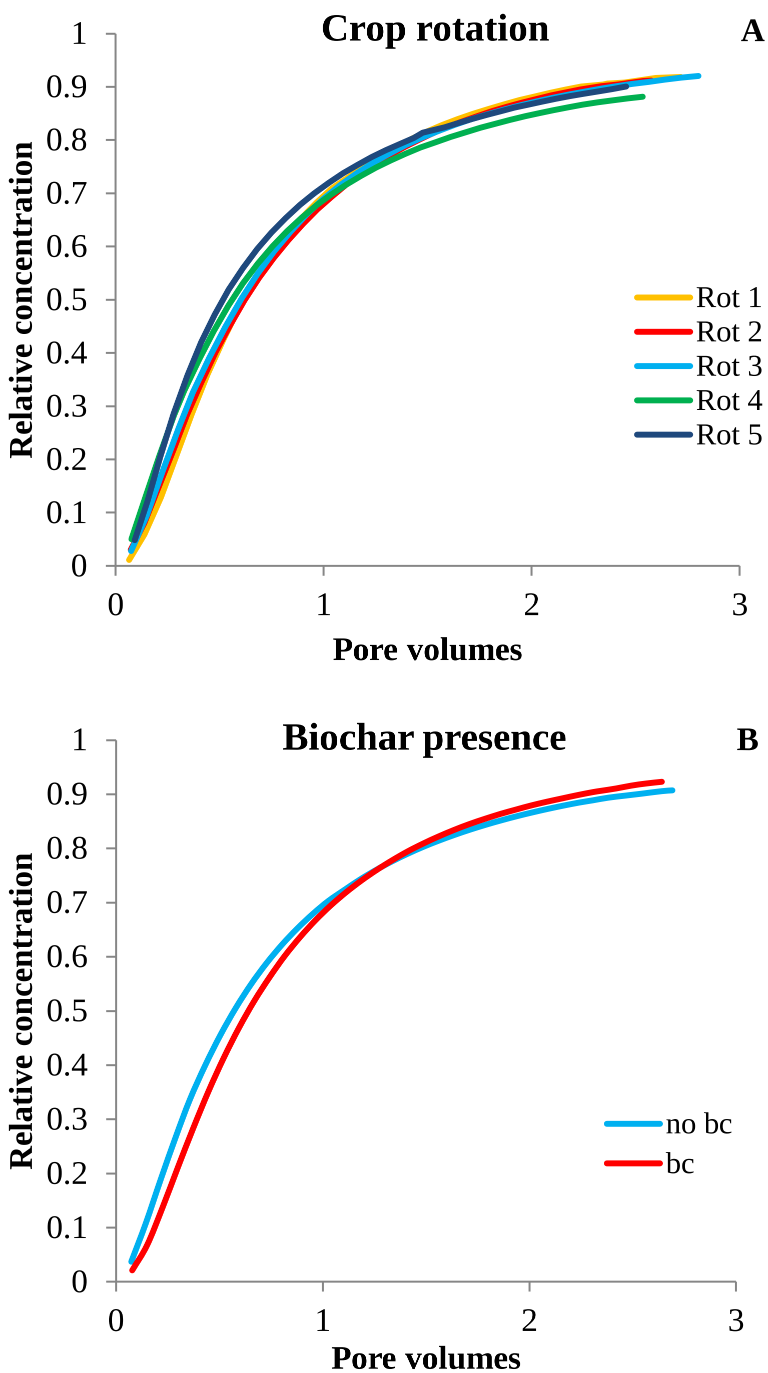

Fig. 1. Calcium chloride breakthrough curves for 2014 saturated steady flow solute transport experiment, cropping rotation (A) and by biochar (bc) to no-biochar treatment (B). Curves represent averages of the model fitted data.

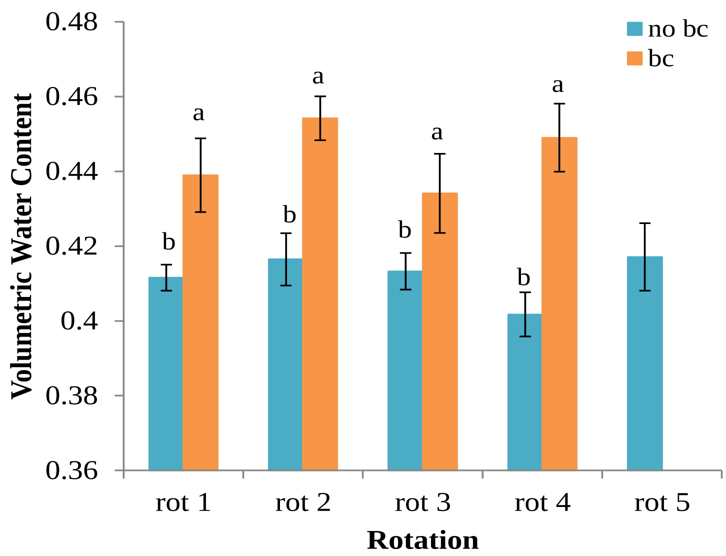

Fig. 2. Gravity drained soil volumetric water content (cm^3 cm^{-3}) by rotation, measured in 2014 on biochar and no-biochar treatments. Values are the average of four field replicates with standard error bars. Different letters indicate significant differences between biochar and no-biochar treatments within a rotation ($P < 0.05$).

Bulk density is an easily measurable and important indicator of soil structure. We observed (2016 cores) a significant decrease in soil bulk density in Rot. 5 compared to Rot. 4 ($P < 0.05$). It was expected that Rot. 5 would have the lowest bulk density because of the greater root biomass found near the soil surface under continuous switchgrass stands. Previous studies have shown lower soil bulk density in systems containing switchgrass or other perennial grasses (Murphy et al., 2004; Schmer et al., 2011). Overall, biochar presence decreased bulk density compared to the control plots (Table 3). Bulk density results for the 2014 samples were confounded by a tillage effect (hence not presented), however, the bulk density results for the 2016 samples are an unbiased measure of the biochar effect on bulk density, because all plots except those in switchgrass were tilled in the spring of 2015. Thus, the 2016 data provide evidence that biochar amendments decrease soil bulk density under field conditions. Further, when the rotations were evaluated independently, biochar significantly lowered bulk density within Rot. 1 (P = 0.025), Rot. 3 (P = 0.015), and Rot. 4 (P < 0.0001). Lastly, although biochar age was not found to have a significant effect on soil bulk density in this study (Table 4), further research is needed from longer-term field experiments to determine whether or not there is a biochar age effect on soil bulk density.

Table 3. Physical and chemical properties measured in 2016. Values are the average of four replicates with standard error and are grouped by crop rotation and biochar. Only no biochar plots were used in comparing crop rotations. Biochar treatment effect (yes, no) does not include Rot. 5 data. Different letters indicate significance between factors within a group (P < 0.05).

Property†	**Crop rotation**					**Biochar treatment**	
	Rot 1	**Rot 2**	**Rot 3**	**Rot 4**	**Rot 5**	**Yes**	**No**
BD, g cm^{-3}	1.386**ab** (0.011)	1.373**ab** (0.020)	1.391**ab** (0.016)	1.410**a** (0.013)	1.325**b** (0.026)	1.340**b** (0.009)	1.390**a** (0.008)
Total C, %	2.016**b** (0.078)	2.124**ab** (0.125)	2.073**b** (0.085)	2.057**b** (0.053)	2.531**a** (0.190)	2.839**a** (0.061)	2.068**b** (0.045)
Total N, %	0.195**b** (0.005)	0.205**ab** (0.010)	0.202**b** (0.007)	0.204**b** (0.004)	0.241**a** (0.016)	0.215**a** (0.003)	0.202**b** (0.004)
C:N ratio, % $\%^{-1}$	10.280**a** (0.180)	10.282**a** (0.142)	10.193**a** (0.122)	10.064**a** (0.085)	10.404**a** (0.132)	13.179**a** (0.164)	10.205**b** (0.069)
pH	6.22**b** (0.059)	6.39**a** (0.054)	6.25**ab** (0.061)	6.04**c** (0.067)	6.04**c** (0.060)	6.40**a** (0.027)	6.22**b** (0.033)
EC, μS cm^{-1}	28.779**b** (1.353)	39.182**a** (3.273)	35.423**a** (2.339)	35.803**a** (1.736)	38.068**a** (3.184)	33.334**a** (1.111)	34.797**a** (1.209)
Extractable P, mg kg^{-1}	32.592**c** (3.371)	40.283**c** (4.297)	37.172**c** (3.580)	51.556**b** (4.726)	82.825**a** (6.174)	40.749**a** (2.506)	40.401**a** (2.138)
Extractable K, mg kg^{-1}	354.642**b** (18.324)	290.408**c** (16.462)	311.424**bc** (15.985)	348.562**b** (22.602)	469.135**a** (31.002)	361.071**a** (11.571)	326.259**b** (9.651)

† BD, bulk density; EC, electrical conductivity; Rot 1, continuous corn; Rot 2, alternating corn-soybean; Rot 3, corn-soybean-triticale/soybean-corn-soybean-triticale/soybean; Rot 4, corn-corn-corn/switchgrass-switchgrass-switchgrass-switchgrass; Rot 5, continuous switchgrass.

To counter the acidifying effects of fertilizers farmers often apply agricultural lime. Soil pH was significantly lower in Rot. 4 and 5 compared to Rot. 1, 2, and 3, and the pH for Rot. 1 was significantly lower than Rot. 2. Rotation 4 was not different from Rot. 5 and Rot. 3 did not differ from Rot. 1 and 2 (Table 3). A lower soil pH for the rotations that include switchgrass reflects the effects of management such as fertilization and biomass harvesting, which accelerates removal of base cations from the soil. This finding differs from results of earlier research where lower soil pH in croplands compared to switchgrass was attributed to soil acidification resulting from long-term N fertilization (Liebig et al., 2005). Nitrogen fertilization rates at the LTRPs vary depending upon both rotation and sequence within a rotation. Rotations 1 and 4 receive 190 kg N ha^{-1} annually, Rot. 2 receives 135 kg N ha^{-1} in corn years only, Rot. 3 receives 135 kg N ha^{-1} in corn and triticale years but no fertilizer in soybean years, and Rot. 5 receives 135 kg N ha^{-1} annually. From 2006-2014, nitrogen was applied as urea, and since spring 2015, it has been applied as encapsulated urea to reduce volatilization loss. We observed a significant biochar rotation interaction, as soil pH increased due to biochar in Rot. 1 ($P = 0.028$), Rot. 3 ($P = 0.045$), and Rot. 4 ($P = 0.0005$). Biochar age had no effect on soil pH (Table 4). This is in agreement with previous work showing that most biochars are a weak agricultural liming agent (Hass et al., 2012). Soil EC was significantly lower in Rot. 1 compared to all other rotations ($P < 0.05$). There was no overall effect of biochar, but a rotation by biochar interaction was found for Rot. 2, as biochar significantly lowered soil EC ($P = 0.02$). These differences were likely associated with management at the site (e.g., crops in rotation) and not inherent soil properties, as no consistent pattern was evident.

Another key indicator of soil quality is total soil organic C (Andrews et al., 2004). As expected biochar significantly increased total soil C ($P < 0.0001$) and the soil C:N ratio ($P < 0.05$) across all rotations relative to the controls. When the no-biochar controls were analyzed by rotation, Rot. 5 had the highest total soil C and this value was significantly higher than rotations 1, 3, and 4 ($P < 0.05$) (Table 3). Further, the 2016 soil C levels for Rot. 5 were significantly higher than soil C levels in all other rotations at the time of site establishment (2006) (Fig. 3). Unfortunately, no data on soil properties were collected from Rot. 5 in 2006 for comparison to the 2016 values, however, the data suggest that continuous switchgrass stands are accumulating soil C relative to other cropping systems. The lack of tillage in the continuous switchgrass rotation may also play a role in the accumulation of soil C. Finally when evaluated by biochar age, within Rot. 1 subplots containing biochar aged 4 yr were significantly higher in soil C than subplots containing biochar aged 3 yr (Table 4). No other differences based on biochar age were observed.

Similar to soil C, total soil N was highest in Rot. 5, which was significantly higher than Rot. 1, 3, and 4 ($P < 0.05$), and higher than N levels at the time of establishment (Fig. 4). This result suggests the building of soil N in continuous switchgrass stands. Furthermore, there was an overall effect of biochar on soil N ($P = 0.0002$) and a biochar age effect within Rot. 1, with soil N for subplots having biochar aged 4 yr significantly higher than those containing biochar aged 3 yr. When assessed by biochar and rotation, biochar increased total soil N across all rotations and a significant biochar rotation interaction was found as soil N was significantly higher in the biochar treatments relative to the no biochar controls in Rot. 1 and 2 only ($P < 0.05$). Furthermore, soil N levels in the biochar plots for all rotations were significantly higher compared to N levels in the baseline (2006) soil samples (Fig. 4). This finding remains consistent even after accounting for the pyrogenic N that was added with the biochar, which contributes 0.0017% N to the total measured soil N in Rot. 1 to 4. Similarly, 0.745% of the total soil C percent for Rot. 1 to 4 is attributable to pyrogenic C. This together with the biochar age effect on soil C observed for Rot. 1, suggests a possible synergistic interaction between biochar and

Table 4. All chemical properties measured from soil cores collected in 2016. Values are the average of four replicates with standard errors, and are grouped by biochar (BC) age within each crop rotation. Different letters indicate significance between years within a rotation ($P < 0.05$).

Property†	**Crop rotation**												
	Rot 1			**Rot 2**		**Rot 3**			**Rot 4**				
	BC 2yr	**BC 3yr**	**BC 4yr**	**BC 3yr**	**BC 4yr**	**BC 2yr**	**BC 3yr**	**BC 4yr**	**BC 1yr**	**BC 2yr**	**BC 3yr**	**BC 4yr**
BD, g cm^{-3}	1.342**a** (0.010)	1.362**a** (0.021)	1.322**a** (0.022)	1.337**a** (0.027)	1.348**a** (0.031)	1.358**a** (0.040)	1.342**a** (0.039)	1.331**a** (0.030)	1.355**a** (0.029)	1.366**a** (0.016)	1.333**a** (0.030)	1.298**a** (0.023)
Total C, %	2.844**ab** (0.132)	2.449**b** (0.141)	3.021**a** (0.185)	2.762**a** (0.206)	2.991**a** (0.169)	2.806**a** (0.223)	2.895**a** (0.231)	2.772**a** (0.204)	2.803**a** (0.172)	2.696**a** (0.130)	2.759**a** (0.201)	3.149**a** (0.262)
Total N, %	0.211**ab** (0.008)	0.197**b** (0.007)	0.217**a** (0.006)	0.216**a** (0.013)	0.225**a** (0.011)	0.217**a** (0.014)	0.219**a** (0.012)	0.209**a** (0.007)	0.225**a** (0.016)	0.207**a** (0.008)	0.213**a** (0.010)	0.217**a** (0.009)
C:N ratio, % %$^{-1}$	13.569**ab** (0.510)	12.383**b** (0.462)	13.899**a** (0.671)	12.685**a** (0.304)	13.271**a** (0.228)	12.851**a** (0.324)	13.104**a** (0.409)	13.214**a** (0.638)	12.517**a** (0.379)	13.112**a** (0.826)	12.881**a** (0.439)	14.500**a** (1.030)
pH	6.43**a** (0.09)	6.41**a** (0.09)	6.33**a** (0.09)	6.42**a** (0.06)	6.50**a** (0.09)	6.38**a** (0.12)	6.45**a** (0.08)	6.39**a** (0.08)	6.22**a** (0.16)	6.45**a** (0.14)	6.34**a** (0.05)	6.29**a** (0.08)
EC, µS cm^{-1}	33.865**a** (3.287)	28.914**a** (1.682)	29.106**a** (2.030)	27.628**b** (1.177)	36.194**a** (2.526)	42.436**a** (8.013)	29.914**b** (2.900)	31.4**ab** (2.252)	31.343**a** (2.595)	44.188**a** (7.086)	36.769**a** (3.025)	34.108**a** (2.700)
Extractable P, mg kg^{-1}	34.963**a** (4.113)	30.028**a** (3.749)	25.380**a** (5.145)	37.626**a** (7.355)	43.220**a** (5.514)	35.701**a** (4.480)	38.013**a** (7.171)	30.047**a** (5.440)	59.457**a** (10.72)	44.592**a** (5.777)	64.934**a** (13.52)	56.631**a** (11.80)
Extractable K, mg kg^{-1}	348.25**a** (38.15)	356.51**a** (36.23)	349.31**a** (20.96)	309.53**a** (24.68)	349.85**a** (12.07)	290.48**a** (11.12)	357.04**a** (47.68)	374.35**a** (49.84)	390.35**ab** (39.51)	283.71**b** (14.12)	456.68**a** (56.32)	474.15**a** (38.79)

† BD, bulk density; EC, electrical conductivity; Rot 1, continuous corn; Rot 2, alternating corn-soybean; Rot 3, corn-soybean-triticale/soybean-corn-soybean-triticale/soybean; Rot 4, corn-corn-corn/switchgrass-switchgrass-switchgrass-switchgrass.

biogenic sources of C and N. Biochar has been shown to alter soil microbial activity (Warnock et al., 2007; Steinbeiss et al., 2009; Lehmann et al., 2011), as no biological indicators were evaluated here, we cannot distinguish whether biotic and abiotic processes contributed to the apparent synergism. However, the results point to biochar helping catalyze the formation of biogenic humic substances and the associated accumulation of N, suggesting a negative priming effect. This finding is consistent with Rogovska et al. (2011) who reported evidence of negative priming when comparing CO_2 emissions from soils amended with manure and manure plus biochar. This relationship between biochar, biochar age, and soil N accumulation is a topic that requires further investigation.

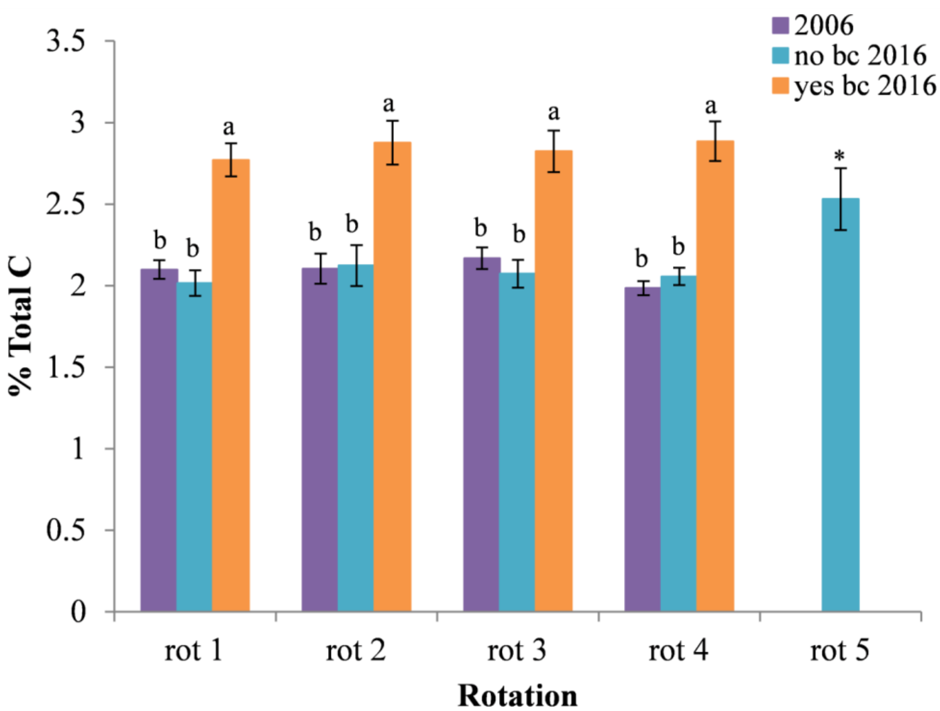

Fig. 3. Total soil C by rotation measured in 2006 and in 2016 for biochar and no-biochar treatments. Values are the average of four field replicates with standard error bars. Different letters indicate significant differences between biochar and no-biochar treatments within a rotation ($P < 0.05$). Significance between Rot. 5 and the no-biochar plots from 2006 and 2016 is indicated by an asterisk (*).

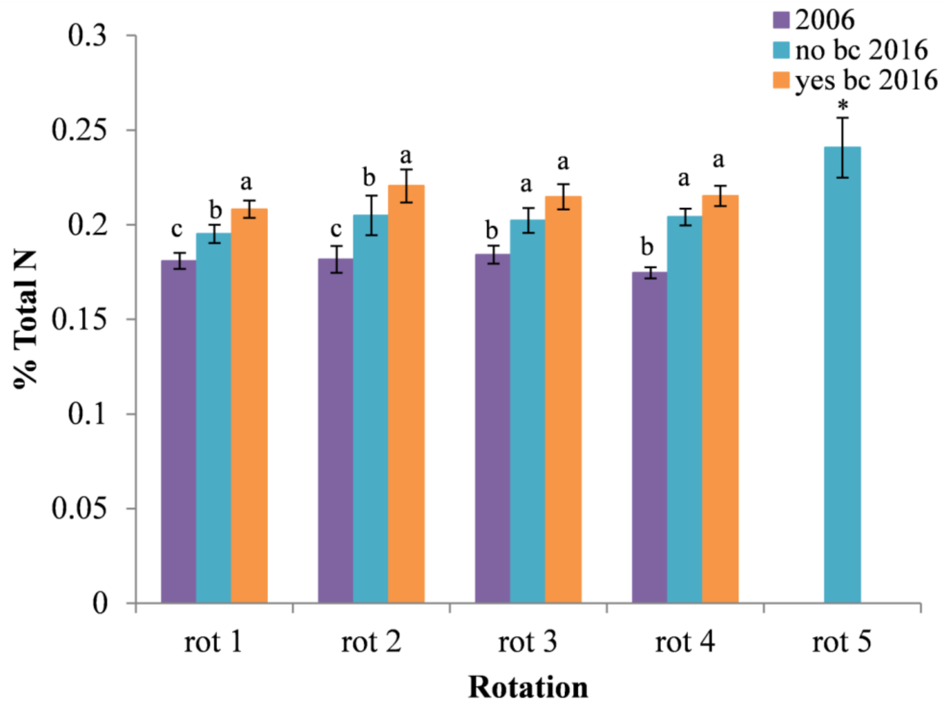

Fig. 4. Effect of crop rotation and biochar (bc) on Total soil N by rotation measured in 2006 and in 2016 for biochar and no-biochar treatments. Values are the average of four field replicates with standard error bars. Different letters indicate significant differences between biochar and no-biochar treatments within a rotation ($P < 0.05$). Significance between Rot. 5 and the no-biochar plots from 2006 and 2016 is indicated by an asterisk (*).

Determining the amount of plant nutrients in the soil is important for understanding their bioavailability to a growing crop. Phosphorus and potassium fertilization rates at the LTRPs were constant from 2006 to 2014 with 67 kg P ha^{-1} and 90 kg K ha^{-1} applied annually to all plots. Soil test results in 2015 revealed very low levels of both soil P and K as determined by the Mehlich-III extraction. As a result, in 2015 all plots except for Rot. 5 (switchgrass) received 190 kg P ha^{-1} and 992 kg K ha^{-1}. Our results suggest that the addition of biochar resulted in no measurable difference in soil P across all rotations and no overall biochar effect. A significant biochar rotation interaction was found for soil K, as biochar increased soil K levels in Rot. 4 only

(P = 0.006). We attribute this to biochar containing some K. This result differs from what has largely been reported by other studies, as a meta-analysis of the biochar literature by Biedermen and Harpole (2013) concluded that biochar on average increases soil P and K. Evaluated by biochar age, soil K concentrations within Rot. 4 were actually lower for biochar aged 2 yr but higher for plots containing biochar aged 3 and 4 yr ($P < 0.05$) and no differences in soil P concentration with biochar age were observed (Table 4). The difference in soil K within Rot. 4 is attributed to management at the site (e.g., crops in rotation), as no clear pattern was evident. Further investigation into soil nutrient dynamics at the LTRPs is needed to clarify these findings.

When soil P and K were analyzed by rotation alone, Rot. 5 had higher values for soil P and K than all other rotations ($P < 0.05$). Switchgrass is a well-known crop for having low management and fertilization requirements (McLaughlin and Kszos, 2005) and it is possible that the increased root biomass in the continuous switchgrass rotation reduces leaching losses and increases nutrient retention. Additionally, removal rates of soil P under switchgrass have been reported to be between 7 and 14 kg P ha^{-1} yr^{-1} (Schmer et al., 2011), which is much lower than the 42 kg P ha^{-1} yr^{-1} removal rates reported for corn and soybean systems (Mallarino et al., 2011). Further, Rot. 4 had greater soil P than rotations 1, 2, and 3 ($P < 0.05$) and Rot. 1 and 4 had higher levels of soil K compared to Rot. 2 (Table 3). Differences in soil P and K levels are likely in response to crop rotation and not fertilizer applications since all rotations, except for Rot. 5, received the same amount of fertilizer. Although, the finding that soil P and K levels were higher in Rot. 5 compared to all other rotations, without the large fertilizer inputs in 2015 is significant.

Conclusions

Our findings indicate that crop rotation, biochar, and biochar age all had an impact on several, but not all, of the soil chemical and physical properties measured in this study. In general, crop rotations containing switchgrass (Rot. 4 and 5) had a positive impact on a greater number of soil quality indicators compared to the conventional cropping systems (Rot. 1 and 2) and a conventional rotation with a cover crop (Rot. 3). Continuous switchgrass contributed to the accumulation of soil C and N, increased retention of P and K, and decreased soil bulk density, but with a possible tradeoff from biomass harvesting leading to lower soil pH. Biochar increased volumetric water content total soil C and N, soil C/N ratio, pH, and plant available K, while decreasing soil bulk density and solute dispersivity. The evidence from the 2016 sampling that total soil C and N continued to increase with biochar age implied a synergistic interaction (negative priming). This finding emphasized the critical importance of including biochar age as a factor in future biochar field studies and the need for more field studies that evaluate longer term, > 4 yr, biochar aging effects on soil quality. The interaction between biochar and crop rotations indicated the complexity of soil quality responses to biochar and the possibility of further synergistic interactions by integrating biochar amendments with management systems that include annual cover crops or perennial biomass crops to enhance C sequestration and sustainability of biomass harvesting. Overall, results supported our stated hypotheses, that the sustainability of bioenergy cropping systems could be enhanced with the incorporation of biochar amendments and alternative crop rotations into the Midwestern landscape.

Acknowledgements

Funding for this research was provided by Global Climate and Energy Project, Stanford Subaward Agreement No. 640 60413992-112883-A, by the USDA National Institute of Food and Agriculture under Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30411, and by the National Science Foundation under EPSCoR Grant Number EPS-1101284.

References

Andrews, S.S., D.L. Karlen, and C.A. Cambardella. 2004. The soil management assessment framework. Soil Sci. Soc. Am. J. 68:1945–1962. doi:10.2136/sssaj2004.1945

Arthur, E., E. Tuller, P. Moldrup, and L. de Jonge. 2015. Effects of biochar and manure amendments on water vapor sorption in a sandy loam soil. Geoderma. 243-244:175-182. doi:10.1016/j.geoderma.2015.01.001

Artiola, J.F., C. Rasmussen, and R. Freitas. 2012. Effects of a biochar-amended alkaline soil on the growth of romaine lettuce and bermudagrass. Soil Sci. 177:561–570. doi:10.1097/SS.0b013e31826ba908

Asbjornsen, H., V. Hernandez-Santana, M. Liebman, J. Bayala, J. Chen, M. Helmers, and L. Schulte. 2013. Targeting perennial vegetation in agricultural landscapes for enhancing ecosystem services. Renew. Agr. Food Syst. 29:101–125. doi.org/10.1017/S1742170512000385

Bakshi, S., D. Aller, D. Laird, and R. Chintala. 2016. Comparison of the physical and chemical properties of laboratory- and field-aged biochars. J. Environ. Qual. 45:1627-1634. doi:10.2134/jeq2016.02.0062

Basso, A., F. Miguez, D. Laird, R. Horton, and M. Westgate. 2013. Assessing potential of biochar for increasing water-holding capacity of sandy soils. GCB Bioenergy. 5:132–143. doi: 10.1111/gcbb.12026

Biederman, L., and W. Harpole. 2013. Biochar and its effects on plant productivity and nutrient cycling: A meta-analysis. GCB Bioenergy. 5:202–214. doi:10.1111/gcbb.12037

Blanco-Canqui, H. 2010. Energy crops and their implications on soil and environment. Agron. J. 102:403-419. doi.org/10.2134/agronj2009.0333

Blanco-Canqui, H. 2013. Crop residue removal for bioenergy reduces soil carbon pools: How can we offset carbon losses? Bioenergy Res. 6:358–371. doi.org/10.1007/s12155-012-9221-3

Blanco-Canqui, H., and R. Lal. 2009. Crop residue removal impacts on soil productivity and environmental quality. Crit. Rev. Plant Sci. 28:139-163. doi:10.1080/07352680902776507

Bot, A., and J. Benites. 2005. The importance of soil organic matter: Key to drought-resistant soil and sustained food and production. ISBN: 92-5-105366-9. UN FAO, Rome. http://www.fao.org/publications/card/en/c/d191e97e-633b-5f2f-a155-eeffbd50541f/

Brewer, C. 2012. Biochar characterization and engineering. Ph.D. dissertation, Iowa State Univ., Ames. http://lib.dr.iastate.edu/etd/12284

Bruun, E. W., C. T. Petersen, E. Hansen, J. K. Holm, and H. Hauggaard-Nielsen. 2014. Biochar amendment to coarse sandy subsoil improves root growth and increases water retention. Soil Use Manage. 30:109-118. doi:10.1111/sum.12102

Bullock, D. 1992. Crop rotation. Crit. Rev. Plant Sci. 11:309–326.

Carter, M. 2002. Soil quality for sustainable land management. Agron. J. 94:38–47. doi:10.2134/agronj2002.3800

Collins, H., P. Rasmussen, and C. Douglas, Jr. 1992. Crop rotation and residue management effects on soil carbon and microbial dynamics. Soil Sci. Soc. Am. J. 56:783-788. doi:10.2136/sssaj1992.03615995005600030018x

Cruse, R., and C. Herndl. 2009. Balancing corn stover harvest for biofuels with soil and water conservation. J. Soil Water Conserv. 64:286–291. doi.org/10.2489/jswc.64.4.286

Dabbert, S., and P. Madden. 1986. The transition to organic agriculture: A multiyear simulation model of a Pennsylvania farm. Am. J. Alternative Agric. 1:107–114. https://doi.org/10.1017/S0889189300001028

Davis, A., J. Hill, C. Chase, A. Johanns, and M. Liebman. 2012. Increasing cropping system diversity balances productivity, profitability and environmental health. PLoS ONE. 7:e47149. doi:10.1371/journal.pone.0047149

Downie, A., A. Crosky, and P. Munroe. 2009. Physical properties of biochar. p. 13–29. *In*: J. Lehmann and S. Joseph (ed.) Biochar for environmental management: Science and technology. Earthscan, London.

Edwards, C. 1989. The importance of integration in sustainable agricultural systems. Agric Ecosyst. Environ. 27:25-35. doi:10.1016/0167-8809(89)90069-8

Gaskin, J.W., A. Speir, L.M. Morris, L. Ogden, K. Harris, D. Lee, and K.C. Das. 2007. Potential for pyrolysis char to affect soil moisture and nutrient status of loamy sand soil. *In*: Georgia Water Resources Conference. University of Georgia. https://smartech.gatech.edu/handle/1853/48168

Giller, K., M. Beare, P. Lavelle, A. Izac, and M. Swift. 1997. Agricultural intensification, soil biodiversity and agroecosystem function. Appl. Soil Ecol. 6:3-16. doi:10.1016/S0929-1393(96)00149-7

Glaser, B., J. Lehmann, and W. Zech. 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal - a review. Biol. Fertil. Soils. 35:219–230. doi:10.1007/s00374-002-0466-4

Hale, S.E., K. Hanley, J. Lehmann, A. Zimmerman and G. Cornelissen. 2011. Effects of chemical, biological, and physical aging as well as soil addition on the sorption of pyrene to activated carbon and biochar. Environ. Sci. Technol. 45:10445-10453. doi:10.1021/es202970x

Halpern, M.T., J.K. Whalen, and C.A. Madramootoo. 2010. Long-term tillage and residue management influences soil carbon and nitrogen dynamics. Soil Sci. Soc. Am. J. 74:1211–1217. doi:10.2136/sssaj2009.0406

Hammerbeck, A., S.J. Stetson, S. Osborne, T. Schumacher, and J. Pikul, Jr. 2012. Impact of corn residue removal on soil aggregate distribution and properties. Soil Sci. Soc. Am. J. 76:1390–1398.

Hardie, M., Clothier, B., Bound, S., Oliver, G., Close, D. 2014. Does biochar influence soil physical properties and soil water availability? Plant Soil. 376:347–361. doi:10.1007/s11104-013-1980-x

Hass, A., J. Gonzalez, I. Lima, H. Godwin, J. Halvorson, and D. Boyer. 2012. Chicken manure biochar as liming and nutrient source for acid Appalachian soil. J. Environ. Qual. 41:1096-1106. doi:10.2134/jeq2011.0124

Heaton, E., F. Dohleman, and S. Long. 2008. Meeting US biofuel goals with less land: the potential of Miscanthus. Glob. Change Biol. 14:2000–2014. doi: 10.1111/j.1365-2486.2008.01662.x

Jeffery, S., M.B. Meinders, C.R. Stoof, T.M. Bezemer, T.F. van de Voorde, L. Mommer, and J.W. van Groenigen. 2015. Biochar application does not improve the soil hydrological function of a sandy soil. Geoderma. 251:47–54. doi.org/10.1016/j.geoderma.2015.03.022

Karlen, D., G. Varvel, D. Bullock, and R. Cruse. 1994. Crop rotations for the 21st century. Adv. Agron. 53:1–45.

Karlen, D.L., E.G. Hurley, S.S. Andrews, C.A. Cambardella, D.W. Meek, M.D. Duffy, and A.P. Mallarino. 2006. Crop rotation effects on soil quality at three northern corn/soybean belt locations. Agron. J. 98:484–495. doi:10.2134/agronj2005.0098

Karlen, D.L., S.J. Birell, and J. Hess, 2011. A five-year assessment of corn stover harvest in central Iowa, USA. Soil Tillage Res. 115:47–55. doi.org/10.1016/j.still.2011.06.006

Kaspar, T., D. Erbach, and R. Cruse. 1990. Corn response to seed-row residue removal. Soil Sci. Soc. Am. J. 54:1112–1117. doi:10.2136/sssaj1990.03615995005400040032x

Katsvairo, T., W. Cox, and H. van Es. 2002. Tillage and rotation effects on soil physical characteristics. Agron. J. 94:299-304. doi:10.2134/agronj2002.2990

Kay, B. 1990. Rates of change of soil structure under different cropping systems. Adv. Soil Sci. 12:1–52

Klute, A., and C. Dirksen. 1986. Hydraulic conductivity and diffusivity: laboratory methods. p. 687-734. *In*: A. Klute (ed.) Methods of Soil Analysis, Part 1. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Laird, D.A. 2008. The Charcoal Vision: a win–win–win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. Agron. J. 100:178–181. doi:10.2134/agrojnl2007.0161

Laird, D.A., P.D. Fleming, D.L. Karlen, B. Wang, and R. Horton. 2010a. Biochar impact on nutrient leaching from a Midwestern agricultural soil. Geoderma 158:436–442. doi.org/10.1016/j.geoderma.2010.05.012

Laird, D.A., P.D. Fleming, D.D. Davis, R. Horton, B. Wang, and D.L. Karlen. 2010b. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. Geoderma 158:443–449. doi: 10.1016/j.geoderma.2010.05.013

Laird, D.A., and C. Chang. 2013. Long-term impacts of residue harvesting on soil quality. Soil Tillage Res. 134:33–40. doi.org/10.1016/j.still.2013.07.001

Lal, R. 2008. Crop residues as soil amendments and feedstock for bioethanol production. Waste Manage. 28:747–758. doi.org/10.1016/j.wasman.2007.09.023

Lal, R. 2015. A system approach to conservation agriculture. J. Soil Water Conserv. 70: 82A-88A. doi:10.2489/jswc.70.4.82A

Langholtz, M.H., B.J. Stokes, and L.M. Eaton. 2016. 2016 Billion-Ton Report: Advancing Domestic Resources for a Thriving Bioeconomy, Volume 1: Economic Availability of Feedstocks. ORNL/TM-2016/160. Oak Ridge National Laboratory, Oak Ridge, TN. http://energy.gov/sites/prod/files/2016/07/f33/2016_billion_ton_report_0.pdf (accessed 14 July 2016)

Lawrinenko, M. and D. Laird. 2015. Anion exchange capacity of biochar. Green Chem. 17:4628-4636. doi:10.1039/c5gc00828j

Lehmann, J., M.C. Rillig, J. Thies, C.A. Masiello, W.C. Hockaday, and D. Crowley. 2011. Biochar effects on soil biota- A review. Soil Biol. Biochem. 43:1812-1836. doi.org/10.1016/j.soilbio.2011.04.022

Liebig, M., H. Johnson, J. Hanson, and A. Frank. 2005. Soil carbon under switchgrass stands and cultivated cropland. Biomass Bioenerg. 28:347–354. doi.org/10.1016/j.biombioe.2004.11.004

Liebman, M., M. Helmers, L. Schulte, and C. Chase. 2013. Using biodiversity to link agricultural productivity with environmental quality: Results from three field experiments in Iowa. Renew. Agr. Food Syst. 28:115–128. doi:10.1017/S1742170512000300

Lim, T.J., K. Spokas, G. Feyereisen, and J. Novak. 2016. Predicting the impact of biochar additions on soil hydraulic properties. Chemosphere. 142:136–144. doi.org/10.1016/j.chemosphere.2015.06.069

Major, J., M. Rondon, D. Molina, S. Riha, and J. Lehmann. 2010. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. Plant Soil. 333:117–128. doi.10.1007/s11104-010-0327-0

Major, J., M. Rondon, D. Molina, S. Riha, and J. Lehmann. 2012. Nutrient leaching in a Colombian savanna Oxisol amended with biochar. J. Environ. Qual. 41:1076–1086. doi:10.2134/jeq2011.0128

Mallarino, A. P., R. R. Oltmans, J. R. Prater, C. X. Villavicencio, and L. B. Thompson. 2011. Nutrient uptake by corn and soybean, removal, and recycling with crop residue. In Proc. 2011 Integrated Crop Management Conference, Iowa State University, Ames, Iowa.

Mann, L., V. Tolbert, and J. Cushman. 2002. Potential environmental effects of corn (*Zea mays* L.) stover removal with emphasis on soil organic matter and erosion. Agric. Ecosyst. Environ. 89:149–166. doi.org/10.1016/S0167-8809(01)00166-9

McLaughlin, S.B., and L.A. Kszos. 2005. Development of switchgrass (*Panicum virgatum*) as a bioenergy feedstock in the United States. Biomass Bioenerg. 28:515–535. doi.org/10.1016/j.biombioe.2004.05.006

Mehlich, A. 1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. Commun. Soil Sci. Plant Anal. 15:1409–1416.

Morgan, R. P, J. N. Quinton, and J. Edwards. 1995. Vegetation strategies for combating desertification. MEDALUS II Project 3 Managing Desertification. Final Report.

Mukherjee, A. and R. Lal. 2013. Biochar impacts on soil physical properties and greenhouse gas emissions. Agronomy 3:313–339. doi:10.3390/agronomy3020313

Mukherjee, A., and R. Lal. 2016. Biochar and soil quality. Encyclopedia of Soil Science, 3rd ed. doi:10.1081/E-ESS3-120053997

Murphy, C., B. Foster, M. Ramspott, and K. Price. 2004. Grassland management effects on soil bulk density. Trans. Kans. Acad. Sci. 107:45-54. doi.org/10.1660/0022-8443(2004)107[0045:GMEOSB]2.0.CO;2

Novak, J.M., I. Lima, B. Xing, J.W. Gaskin, C. Steiner, K.C. Das, M. Ahmedna, D. Rehrah, D.W. Watts, W.J. Busscher, and H. Schomberg. 2009. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. Ann. Environ. Sci. 3:195–206.

Ola, A., I.C. Dodd, and J.N. Quinton. 2015. Can we manipulate root system architecture to control soil erosion? Soil. 1:603–612. doi.org/10.5194/soil-1-603-2015.

Parker, J.C., and van Genuchten, M.Th, 1984. Determining Transport Parameters from Laboratory or Field Tracer Experiments, Bulletin 84–3. Virginia Agriculture Experiment Station, Blacksburg, Virginia 95pp.

Perlack, R.D., L.L. Wright, A.F. Turhollow, R.L. Graham, B.J. Stokes, and D.C. Erbach. 2005. Biomass as feedstock for a bioenergy and bioproducts industry: The technical feasibility of a billion-ton annual supply. DOE/USDA Tech. Rep. DOE/GO-102005–2135 ORNL/TM-2005/66. www.ornl.gov/~webworks/cppr/y2001/rpt/123021.pdf[verified 23 Oct. 2007]. USDOE, Office of Scientific & Technical Information, Oak Ridge, TN.

Perlack, R.D., and B.J. Jones. 2011. U.S. billion-ton update: Biomass supply for a bioenergy and bioproducts industry. ORNL/TM-2011/224. Oak Ridge Natl. Lab., Oak Ridge, TN. https://bioenergykdf.net/content/billiontonupdate (accessed 14 July 2016).

Qian, L. and B. Chen. 2014. Interactions of aluminum with biochars and oxidized biochars: Implications for the biochar aging process. J. Agri. Food Chem. 62: 373-380. doi:10.1021/jf404624h

Robinson, C.A., R.M. Cruse, and K.A. Kohler. 1994. Soil management. p. 109–134. *In*: J.L. Hatfield and D.L. Karlen (ed.) Sustainable agriculture systems. Lewis Publ. CRC Press, Boca Raton, FL.

Rogovska, N., D.A. Laird, R. Cruse, P. Fleming, T. Parkin, and D. Meek. 2011. Impact of biochar on manure carbon stabilization and greenhouse gas emissions. Soil Sci. Soc. Am. J. 75:871-879. doi:10.2136/sssaj2010.0270

Rogovska, N., D.A. Laird, S.J. Rathke, and D.L. Karlen. 2014. Biochar impact on Midwestern Mollisols and maize nutrient availability. Geoderma 230-231:340-347. doi.org/10.1016/j.geoderma.2014.04.009

Rogovska, N., D.A. Laird, and D.L. Karlen. 2016. Corn and soil response to biochar application and stover harvest. Field Crop Res. 187:96-106. doi.org/10.1016/j.fcr.2015.12.013

Rondon, M.A., J. Lehmann, J. Ramírez, and M. Hurtado. 2006. Biological nitrogen fixation by common beans (*Phaseolus vulgaris* L.) increases with bio-char additions. Biol. Fertil. Soils. 43:699–708. doi.10.1007/s00374-006-0152-z

Russell, A.E., D.A. Laird, T. Parkin, and A.P. Mallarino. 2005. Impact of nitrogen fertilization and cropping system on carbon sequestration in Midwestern Mollisols. Soil Sci. Soc. Am. J. 69:413–422. doi:10.2136/sssaj2005.0413

Russell, A.E., D.A. Laird, and A.P. Mallarino. 2006. Nitrogen fertilization and cropping system impacts on soil quality in Midwestern Mollisols. Soil Sci. Soc. Am. J. 70:249-255. doi:10.2136/sssaj2005.0058

SAS Institute. 2013. SAS for Windows 9.4. SAS Inst. Inc., Cary, NC.

Schmer, M., M. Liebig, K. Vogel, and R. Mitchell. 2011. Field-scale soil property changes under switchgrass managed for bioenergy. GCB Bioenergy 3:439–448. doi:10.1111/j.1757-1707.2011.01099.x.

Skaggs, T.H., D.B. Jaynes, R.G. Kachanoski, P.J. Shouse, and A.L. Ward. 2002. Solute transport: Data analysis and parameter estimation. In: J.H. Dane and C. Topp, editors, Methods of soil analysis. Part 4. SSSA, Madison, WI. p. 1403–1434.

Steinbeiss, S., G. Gleixner, and M. Antonietti. 2009. Effect of biochar amendment on soil carbon balance and soil microbial activity. Soil Biol. Biochem. 6:1301–1310. doi.org/10.1016/j.soilbio.2009.03.016

Steiner, C., B. Glaser, W. Teixeira, J. Lehmann, W. Blum, and W. Zech. 2008. Nitrogen retention and plant uptake on a highly weathered central Amazonian Ferralsol amended with compost and charcoal. J. Plant Nutr. Soil Sci. 171:893-899. doi:10.1002/jpln.200625199

Stetson, S.J., S.L. Osborne, T.E. Schumacher, A. Eynard, G. Chilom, J. Rice, K.A. Nichols, and J.L. Pikul. 2012. Corn residue removal impact on topsoil organic carbon in a corn-soybean rotation. Soil Sci. Soc. Am. J. 76:1399–1406. doi:10.2136/sssaj2011.0420

Streubel, J.D., H.P. Collins, M. Garcia-Perez, J. Tarara, D. Granatstein, and C.E. Kruger. 2011. Influence of contrasting biochar types on five soils at increasing rates of application. Soil Sci. Soc. Am. J. 75:1402–1413. doi:10.2136/sssaj2010.0325

Tang, G., M.A. Mayes, J.C. Parker and P.M. Jardine. 2010. CXTFIT/Excel-a modular adaptable code for parameter estimation, sensitivity analysis, and uncertainty analysis for laboratory and field tracer experiments. Comput. Geosci. 36:1200–1209. doi:10.1016/j.cageo.2010.01.013

Thies, E., and M. Rilling. 2009. Characteristics of biochar: biological properties. p. 95-105. *In* J. Lehmann and S. Joseph (ed.) Biochar for environmental management: Science and technology. Earthscan, London.

Thies, J., M. Rillig, and E. Graber. 2015. Biochar effects on the abundance, activity, and diversity of soil biota. p. 327-389. *In*: J. Lehmann and S. Joseph (ed.) Biochar for Environmental Management: Science, Technology and Implementation. 2nd Edition. Routledge, New York.

Tilman, D., K.G. Cassman, P.A. Matson, R. Naylor, and S. Polasky. 2002. Agricultural sustainability and intensive production practices. Nature 418:671-677. doi.org/10.1038/nature01014

Uzoma, K.C., M. Inoue, H. Andry, A. Zahoor, and E. Nishihara. 2011. Influence of biochar application on sandy soil hydraulic properties and nutrient retention. J. Food Agric. Environ. 9:1137–1143.

Verheijen, F., S. Jeffery, A.C. Bastos, M. van der Velde, and I. Diafas. 2010. Biochar application to soils: a critical scientific review on effects on soil properties processes and functions. Joint Research Center (JRC), Scientific and Technical Report. Office for the Official Publications of the European Communities, Luxemberg.

Warnock, D.D., J. Lehmann, T.W. Kuyper, and M.C. Rillig. 2007. Mycorrhizal responses to biochar in soil-concepts and mechanisms. Plant Soil. 300:9-20. doi.org/10.1007/s11104-007-9391-5

Wilhelm, W.W., J.M.F. Johnson, J.L. Hatfield, W.B. Voorhees, and D.R. Linden. 2004. Crop and soil productivity response to corn residue removal: A literature review. Agron. J. 96:1–17. doi:10.2134/agronj2004.1000

Wilhelm, W.W., J.R. Hess, D.L. Karlen, J.M.F. Johnson, D.J. Muth, J.M. Baker, H. Gollany, J. Novak, D. Stott, and G. Varvel. 2010. Balancing limiting factors and economic drivers for sustainable Midwestern US agricultural residue feedstock supplies. Ind. Biotechnol. 6:271–287. doi:10.1089/ind.2010.6.271

Yates, F. 1954. The analysis of experiments containing different crop rotations. Biometrics. 10:324–346. doi: 10.2307/3001589

CHAPTER 4. IMPACTS OF FRESH AND AGED BIOCHARS ON PLANT AVAILABLE WATER AND WATER USE EFFICIENCY

Modified from a manuscript published in Geoderma

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Abstract

The ability of soils to hold sufficient plant available water (PAW) between rainfall events is critical to crop productivity. Most studies indicate that biochar amendments decrease soil bulk density and increase soil water retention. However, limited knowledge exists regarding biochars ability to influence PAW and water use efficiency (WUE), and even less is known about the effects of aged biochars on PAW and WUE. This greenhouse study investigated the influence of six fresh and six aged biochars on PAW and WUE for three soils of contrasting texture. PAW and WUE were assessed by growing maize in repacked soil columns (1 kg soil). Plant and water data were collected from the V1 growth stage until the plants died of water stress. Relative to the controls, both fresh and aged biochars increased soil moisture retention in the clay loam soil, had no impact in a silt loam soil, and had variable effects in a sandy loam soil. Final biomass weight increased with the addition of fresh biochar in the sandy loam and silt loam soils and decreased in the clay loam soil, while aged biochar increased biomass weight in the silt loam soil. Both fresh and aged biochars decreased PAW in the clay loam soil and had no impact on PAW in the silt loam soil. Fresh biochar increased PAW, while aged biochar had no effect on PAW for the

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sandy loam soil. WUE decreased in response to both fresh and aged biochars in the clay loam soil and was variable for the other two soils. Results of this experiment indicate that biochar type and biochar age have variable impacts on PAW and WUE, indicating that biochar amendments can improve soil water relations and crop growth under water limited conditions for some but not all soils.

Keywords: Biochar, Biochar age, Soil water retention, Rainfed agriculture, Water stress

Abbreviations: SP, slow pyrolysis; FP, fast pyrolysis; SG, switchgrass; CS, corn stover; SB, soybean; HW, hardwood; PAW, plant available water; WUE, water use efficiency; PWP, permanent wilting point; FC, field capacity; BD, bulk density; WDPT, water droplet penetration test

Introduction

Over 80% of cropland and 60% of food produced globally is the result of rainfed agricultural production (FAO, 2011). This makes getting ‘more crop per drop’ (FAO, 2003) in a period of rapid population growth, increasing environmental degradation, and greater climatic variability a high priority. Managing water efficiently in rainfed systems to maintain high productivity will be essential in order to meet food, fiber, and fuel demands of a growing global population with increasingly variable rain events (IWMI, 2007). Rainfall patterns are expected to change in terms of intensity, frequency, and distribution as the global climate changes (IPCC, 2007). Water is already considered the limiting factor for attaining the maximum yield potential in areas where rainfed agriculture is practiced (Rockstrom et al., 2010). Hence, technologies that improve not only soil water retention but water use efficiency (WUE) and plant available water (PAW) in rainfed systems are critically needed to increase the resilience of food production. This is especially true during critical periods of the growing season when significant yield declines may occur due to limited water availability. One technology currently available that has the potential to improve water management in rainfed agriculture is biochar. Biochar, the solid co-product of biomass pyrolysis, is a soil amendment effective at improving soil water retention while simultaneously sequestering carbon and enhancing soil quality (Lehmann and Joseph, 2009).

Numerous studies indicate that biochar impacts soil water retention and other hydrologic functions, but due to different experimental conditions (including soil type and biochar treatments), results have been variable (Glaser et al., 2002; Major et al., 2012; Jeffery et al., 2015; Hardie et al., 2014; Obia et al., 2016; Lim et al., 2016). Nevertheless, due to the high internal porosity and the large surface area of biochars studies in general support decreased soil bulk density and increased porosity and water retention (Novak et al., 2009; Streubel et al., 2011; Artiola et al., 2012; Basso et al., 2013; Abel et al., 2013; Rogovska et al., 2014; Ma et al., 2016). These many studies have investigated the effects of different biochar and soil mixtures on water retention and soil physical properties but only more recently have a few studies examined biochars influence on PAW and WUE. Quantifying WUE and PAW impacts of biochar in addition to water retention is essential because more water retained in the soil profile does not necessarily equate to more water for a growing plant (Verheijen et al., 2010) and in order to achieve maximum yield potentials plants must be able to access the water.

Very little is known about how biochar aging (weathering) influences PAW and WUE. Although considerable knowledge now exists about how biochar properties change over time, and was recently summarized in Mia et al. (2017), knowledge of how aged biochars in diverse soils influences PAW and WUE remains limited. Biochar age should be considered in biochar studies because although biochars are inherently more recalcitrant than other forms of organic matter, biochar properties still change over time (Downie et al. 2009; Kasozi et al., 2010; Kuzyakov et al., 2014). These changes have been shown to influence biochars' impact on agroecosystem functions (Seredych and Bandosz, 2007, Major et al., 2010; Wang et al., 2012; Borchard et al., 2014; Rajapaksha et al., 2016).

The aging of biochar can be broadly classified as either short- or long- term aging. Short-term aging refers to the hydration and oxidation of biochar surfaces that occurs after exposure to air and moisture (IBI, 2014). Long-term aging results from the physical and biochemical breakdown of biochar particles, dissolution of soluble salts and organic compounds, sorption of dissolved compounds from the soil solution, and the neutralization of alkalis over time in soil environments (Mia et al., 2017). Natural field aging of biochar can take decades to centuries so rapid laboratory aging procedures have been developed to mimic long-term field weathering processes. These artificial procedures often include a combination of acidification, oxidation, and incubations of different biochars (Hale et al., 2011; Uchimiya et al., 2011; Liu et al., 2013; Shi et al., 2015; Bakshi et al., 2016). The presence of aged biochars in soils may be more beneficial than fresh biochars as the changes in physicochemical properties of the biochars that occur on aging may increase the capacity of soils to retain water and nutrients (Mia et al., 2017).

This study was undertaken to assess the impact of artificially aged biochars on soil water relations and crop growth in diverse soils. While we recognize that artificially aged biochars may not be fully representative of naturally aged biochars, they provide a basis for assessing the direction and potential impact of aging on water relations. The objectives of this study were to investigate the influence of biochar age, biochar type, and their interaction on PAW and WUE in maize for three soils with contrasting textures. We hypothesized that biochar amendments would increase PAW and WUE in all three soils and that aged biochars would lead to greater increases in PAW and WUE than their fresh counterparts.

Material and Methods

This greenhouse column experiment was conducted at Iowa State University during the winter of 2015/2016. It involved 39 different treatments with four replicates totaling 156 columns in a complete randomized design. Treatments included 12 different biochars, three soil types, one biochar application rate, one crop, and one watering regime.

Soils

The soils used in this study were collected from three different locations across the state of Iowa and included a sandy loam, a silt loam, and a clay loam (USDA textural classification). Silt loam and clay loam soils were collected from agricultural fields in southwest and central Iowa, respectively, and the sandy loam from a river flood plain in central Iowa. Chemical and physical properties of the three soils are provided in Table 1. Following collection, soils were air dried, sieved to < 2 mm, and stored in sealed plastic containers until the start of the experiment.

Table 1. Soil chemical and physical properties

Property	**Soil type**		
	Sandy loam	Silt loam	Clay loam
pH	7.34	6.80	6.92
EC (µs cm^{-1})	154.3	417	29.1
Extractable P (mg kg^{-1})	39.11	169.60	79.49
Extractable K (mg kg^{-1})	59.48	536.03	369.25

Table 1. Continued

NH^{4+}-N (mg N kg^{-1})	1.90	5.77	7.17
NO^{3-}- N (mg N kg^{-1})	0.37	3.84	3.77
Total C (%)	1.25	2.89	4.86
Total N (%)	0.08	0.29	0.37
% Sand	77.6	14.3	40.7
% Silt	12.5	59.8	29.8
% Clay	9.9	25.9	29.5

Biochars

The biochars used in this study were produced by either fast pyrolysis (FP) or slow pyrolysis (SP) using corn stover (CS), switchgrass (SG), soybean (SB), and hardwood (HW) feedstocks. A subsample of each biochar was aged in the laboratory using acidification and oxidation treatments, followed by incubation with dissolved organic carbon (Bakshi et al., 2016). Briefly, fresh biochars (sieved < 1 mm) were incubated for one month at 40 °C in 1 M HCl (biochar: 1 M HCl = 1:5) with weekly additions of 30% H_2O_2. Following this incubation period biochars were washed twice with 1 M $CaCl_2$, washed with double deionized water, and then incubated for another month at 40 °C in an aqueous solution of dissolved organic carbon extracted from compost. Lastly, the incubated biochars were washed again with double deionized water, air dried, and stored for later use. A brief description of the 12 biochars (six fresh and six aged) used is provided in Table 2. For the complete physiochemical properties of the fresh and aged biochars please refer to Bakshi et al. (2016).

Table 2. Feedstock and production conditions of the six fresh and six aged biochars used in this study (adapted from Bakshi et al., 2016).

Biomass Feedstock	Pyrolysis technique	Pyrolysis temperature (°C)	Source
Hardwood	Fast	600-650	Dynamotive Energy Systems, Richmond, CA
Hardwood	Slow	500-550	Cowboy Charcoal, Brentwood, TN, USA

Table 2. Continued

Soybean	Fast	500	BioCentury Research Farm, Boone, IA, USA
Switchgrass	Slow	500	Iowa State University, Ames, IA, USA
Corn Stover	Fast	500	Avello Bioenergy, Boone, IA, USA
Corn Stover	Slow	500	Iowa State University, Ames, IA, USA

Experimental Design

Previously constructed soil columns made of PVC pipe were used. Each column had dimensions of 14.1 cm high and 10.3 cm diameter, and was fitted with an endcap containing a 12.7 mm diameter hole. Prior to the experiment, the mass of all empty columns was recorded and a small piece of landscape fabric was placed on the underside of each column to allow water flow but prevent any loss of soil material. A Whatman 42 filter paper was placed inside the bottom of the each column to trap soil particles and 100 g of coarse sand (2-5 mm) was added on top of the filter paper to maintain adequate drainage out the bottom of each column. Individual masses of fabric and filter paper were recorded for all columns. The soil and biochar for each treatment were mixed together in a rotary cement mixer for 5 min. Biochar was incorporated at a rate of 1% w w^{-1} for all treatments (field application rate of ~22 t ha^{-1}), after taking into account the moisture content of each soil and biochar. All columns were packed with 1 kg of soil + biochar mixture and manually tapped down to consolidate the soil.

After all 156 columns were packed, they were placed into plastic bins and saturated from the bottom-up with distilled water. Complete saturation was assumed after a head of water was visible on the soil surface. Once saturated, columns were removed from the bins and left to freely drain until the head of water had disappeared (< 30 mins). Extenders, 5 cm high and of a known mass, were secured to the top of the columns containing the clay loam soil (to accommodate the swelling clay) and 70 g of plastic beads were added on top of the soil to serve as mulch and to reduce water loss to evaporation. Soil evaporation curve data was collected as the columns were left to freely drain and weighed at 12, 24, and 48 h, and then every 48 h for eight days. Field capacity (FC) was determined as the weight after 24 h.

After gathering data on soil water evaporation, beads were removed, columns were fertilized with 75 mL of Miracle-Gro® all-purpose plant food (720 g L^{-1}). Additional water was added as needed to bring the columns back to FC and three maize seeds were planted in each column. Soil bulk density (BD) measurements were subsequently taken by measuring the depth from the top of the column to the soil surface as described by Rogovska et al. (2011). Mean and standard error values of BD for each treatment were derived from three replications.

From planting to the V1 growth stage all soil columns were watered to FC every two days to ensure maize emergence. Once seedlings reached the V1 growth stage, plants were thinned to one plant per column (largest plant kept), the columns were watered to FC, and subsequently no water was applied for the duration of the experiment. The plastic beads were added back to their respective column and columns were weighed at 12, 24, and 48 h, and then every 48 h until plant death by moisture stress. The experiment lasted approximately 30 days from the time of the final watering to the final weighing. The change in soil water content (g g^{-1}) over time was recorded along with plant growth stage. PAW of each soil column was determined as the difference in column weight at FC and at final weighing. All PAW values calculated from the greenhouse dry-down experiment are reported on a gravimetric basis (g g^{-1}), because BD was continuously changing during the dry-down experiment. Final soil BD was measured using the same method as described above. Final above ground biomass weight and height were determined at the end of the experiment. WUE was determined from the ratio of final above ground biomass weight to cumulative evapotranspiration.

Soil Water Retention Curves

Soil water retention curves were determined on the soils from each column. A hose connected to the house air system was plugged into the bottom of each column and the soil core was removed intact by air pressure. Subsequently, a metal ring of soil (3.7 cm high and 5.3 cm diameter) was collected from the middle of each soil core for soil water retention analysis. Water retained at -0.33, -1, -3, -5, and -15 bars matric potential were determined using the pressure plate method (Klute, 1986) and a Ceramic Plate Extractor (Soil Moisture Equipment Corp., Santa Barbara, CA, USA). The metal rings were used to determine water retained at -0.33 and -1 bars while rubber rings, 1 cm high and 3 cm diameter, were used to determine water retained at -3, -5, and -15 bars.

Soil within the metal rings were saturated from the bottom with 0.001 M $CaCl_2$ overnight at 20 °C. Saturated samples were weighed, placed into the chamber and pressure set to -0.33 bar. Once no more water was visibly draining from the chamber, the metal rings were weighed, and the same samples were placed back into the chamber and pressure set to -1 bar. Following the collection of sample weight after -1 bar, soil was removed from the metal rings, sieved to < 2 mm, and a subsample was taken for moisture content determination. Rubber rings were filled with the remaining sieved soil and saturated as described previously. After drainage stopped from the chambers set at each pressure potential (-3, -5, and -15 bars), soil was removed from the rubber rings, weighed, oven dried at 105 °C overnight, and reweighed to determine water content. PAW of each sample was determined as the difference in water content held between -0.33 and -15 bars. All PAW values calculated from the laboratory water retention curves are reported on a volumetric basis (cm^3 cm^{-3})

Water Drop Penetration Test

The water drop penetration test (WDPT) was used to evaluate the degree of hydrophobicity of the six fresh and six aged biochars used in this study. The method and classification system described in Dekker et al. (2009) was used; which was originally developed to assess soil water repellency. In triplicate determination, 50 mL of biochar was placed into weigh boats and left in a 50 °C incubator for two weeks. Samples were removed from the incubator, the biochar surface was levelled, and using a plastic transfer pipette three drops of distilled water were placed on the surface. A stopwatch was used to record the time (s) elapsed from when a single water droplet touched the biochar surface to when it was absorbed. The classification of biochar hydrophobicity was based on the time needed to completely penetrate the biochar surface. After completion of the test the biochars were transferred to French square bottles and 100 mL of distilled water was added. Samples were shaken on a reciprocating shaker for 48 h, filtered using Whatman 42 filter paper, and placed back into the 50 °C incubator for two more weeks. After the second drying period the WDPT was repeated as previously described. Two classifications of biochar hydrophobicity are reported: one after the initial drying period and the other after the subsequent wetting-drying period.

Statistical Analysis

Statistical analysis for initial and final soil BD, greenhouse and laboratory PAW, WUE, and final biomass height and weight were performed in R, version 3.3.1. A three-way analysis of variance (ANOVA) was used to assess the interaction effect of biochar age, biochar type (determined by the combination of feedstock and pyrolysis technique), and soil type. All interactions with soil type were significant ($P < 0.0001$) therefore, the individual effects of biochar age and biochar type and their interactions within each soil type were analyzed using a two-way ANOVA. Differences between treatments within each soil type were analyzed using lsmeans. Statistical significance was assessed at the 5% alpha level using the Tukey HSD test. All data are means of four replicates.

Results and Discussion

Bulk Density

Initial BD was not affected by biochar or biochar age in any of the soils (Table 3). However, biochar type and soil type did impact initial BD (Table 4). Initial BD was 1.16, 1.00, and 1.42 (g cm^{-3}) for the silt loam, clay loam, and sandy loam soils, respectively.

Significant interactions of biochar type with soil type and biochar age with soil type were found for final BD (Table 4). Final BD was lower in the biochar treated columns relative to the controls for each soil type and both fresh and aged biochar, with the exception of aged biochar in the sandy loam soil, which was equal to the control (Table 3). Soil columns containing sg.sp biochar had the lowest BD within each soil type (data not shown).

The lack of a biochar impact on initial BD can be attributed to the way in which the columns were prepared, targeting a common BD for each soil type. During the course of the study soil consolidation increased the final soil BD relative to the initial BD, due to the effects of gravity and moisture loss over time. Our results indicate that the increase in BD with time was less for the biochar treated columns compared to the controls, which is consistent with other studies (Laird et al., 2010; Burrell et al., 2016).

Table 3. Soil and plant properties measured from each soil column. Values are the average of four replicates with standard errors. Different letters indicate significance between biochar (BC) ages (Fresh BC and Aged BC) and the control by soil type (P < 0.05).

Property	Soil type								
	Sandy loam			Silt loam			Clay loam		
	Control	Fresh BC	Aged BC	Control	Fresh BC	Aged BC	Control	Fresh BC	Aged BC
Initial BD (g cm^{-3})	1.44**a** (0.016)	1.41**a** (0.008)	1.43**a** (0.008)	1.19**a** (0.009)	1.16**a** (0.005)	1.15**a** (0.007)	0.99**a** (0.001)	1.00**a** (0.019)	0.99**a** (0.005)
Final BD (g cm^{-3})	1.56**a** (0.012)	1.53**b** (0.008)	1.56**a** (0.008)	1.53**a** (0.018)	1.48**b** (0.008)	1.47**b** (0.008)	1.66**a** (0.012)	1.63**b** (0.008)	1.61**b** (0.004)
WUE (mg g^{-1})	2.48**a** (0.058)	2.41**a** (0.099)	2.50**a** (0.074)	3.50**a** (0.103)	3.75**a** (0.083)	3.81**a** (0.072)	4.17**a** (0.072)	3.18**b** (0.069)	3.36**b** (0.084)
Final biomass weight (g)	0.478**b** (0.011)	0.564**a** (0.019)	0.473**b** (0.008)	1.021**b** (0.019)	1.106**a** (0.017)	1.113**a** (0.017)	1.554**a** (0.018)	1.381**b** (0.025)	1.496**a** (0.027)
Final biomass height (cm)	53.13**a** (0.921)	54.98**a** (0.872)	52.81**a** (0.588)	68.88**a** (0.875)	67.46**a** (1.250)	70.15**a** (0.831)	73.63**a** (2.461)	71.79**a** (0.907)	72.23**a** (1.504)

Table 4. Results of three-way ANOVA for individual and interaction effects of biochar age (BCage), biochar type (BCtype), and soil type (soil) on plant and soil properties.

Factors	Initial BD		Final BD		Greenhouse PAW		Laboratory PAW		WUE		Biomass weight		Biomass height	
	F-value	*p*-value	*F*-value	*p*-value	*F*-value	*p*-value	*F*-value	*p*-value	*F*-value	*p*-value	*F*-value	*p*-value	*F*-value	*p*-value
soil	1330.36	<0.0001	297.90	<0.0001	2888.48	<0.0001	2241.19	<0.0001	236.19	<0.0001	1787.09	<0.0001	195.09	<0.0001
BCtype	5.53	<0.0001	12.18	<0.0001	11.19	<0.0001	4.479	<0.001	8.07	<0.0001	7.82	<0.0001	0.21	NS
BCage	0.01	NS	0.01	NS	21.13	<0.0001	36.00	<0.0001	4.31	<0.05	0.67	NS	0.15	NS
BCtype*soil	1.48	NS	2.55	<0.01	6.82	<0.0001	3.84	<0.0001	4.70	<0.0001	2.65	<0.01	0.88	NS
BCage*soil	2.19	NS	6.13	<0.01	37.89	<0.0001	15.74	<0.0001	0.42	NS	19.79	<0.0001	2.79	NS
BCage*BCtype	1.59	NS	1.78	NS	4.99	<0.001	3.46	<0.01	2.41	<0.05	1.94	NS	1.14	NS
BCage*BCtype*soil	1.32	NS	0.33	NS	4.77	<0.0001	3.74	<0.001	3.71	<0.001	0.77	NS	1.01	NS

Biochar Hydrophobicity

The WDPT was conducted to assess biochar water repellency. Results indicate that the relative degree of biochar hydrophobicity decreased for all biochars following exposure to a drying-wetting-drying cycle (Table 5). After the first drying period and WDPT (time 1) seven out of twelve biochars were classified as having some degree of hydrophobicity and five were classified as hydrophilic. The second wetting-drying period and WDPT (time 2) resulted in eight of the twelve biochars being classified as hydrophilic and four with hydrophobic properties (Table 5). These findings are consistent with studies that have measured biochar hydrophobicity following exposure to post-pyrolysis wetting and drying treatments (Kinney et al., 2012; Das and Sarmah, 2015). Furthermore, results indicate that all fresh biochars were more hydrophobic than their aged counterparts, which is consistent with the literature (Mia et al., 2017). Feedstock and production technique are likely to also influence biochars' ability to uptake water (Gray et al., 2014), however, based on the qualitative measure used here we cannot accurately distinguish these effects. Overall, the WDPT results indicate that aged biochars are more hydrophilic then fresh biochars and that after additional wetting/drying treatments biochars become less hydrophobic.

Table 5. Classification of biochar hydrophobicity after drying (time 1) and a second wetting-drying period (time 2) for all biochars.

Biochar[a]	Time 1 (s)	Classification 1	Time 2 (s)	Classification 2
fresh-sg.sp	> 600	severely hydrophobic	0-5	hydrophilic
fresh-cs.sp	> 600	severely hydrophobic	< 60	slightly hydrophobic
fresh-cs.fp	60-120	strongly hydrophobic	0-5	hydrophilic
fresh-sb.fp	> 3600	extremely hydrophobic	< 60	slightly hydrophobic
fresh-hw.sp	> 3600	extremely hydrophobic	< 60	slightly hydrophobic
fresh-hw.fp	> 3600	extremely hydrophobic	750	severely hydrophobic
aged-sg.sp	0	hydrophilic	0	hydrophilic

Table 5. Continued

aged- cs.sp	0	hydrophilic	0	hydrophilic
aged- cs.fp	0	hydrophilic	0	hydrophilic
aged- sb.fp	0	hydrophilic	0	hydrophilic
aged- hw.sp	10	slightly hydrophobic	5	hydrophilic
aged- hw.fp	5	hydrophilic	0-5	hydrophilic

[a] biochar abbreviations - fresh biochar (fresh), aged biochar (aged), slow pyrolysis (sp), fast pyrolysis (fp), switchgrass (sg), corn stover (cs), soybean (sb), hardwood (hw).

Greenhouse - Gravimetric Soil Water Content and PAW

Soil water content and PAW (measured gravimetrically because BD changed during the course of the dry-down experiment) for the greenhouse soil columns were affected by biochar age, biochar type, and soil type. Results of the ANOVA show a three-way interaction and individual effects on greenhouse PAW (Table 4). For the silt loam soil, the soil moisture dry-down curves were little affected by biochar and biochar age (Fig. 1). Within the fresh and aged biochars no differences were found for PAW based on biochar type. However, fresh cs.fp had higher PAW and fresh sb.fp lower PAW than their aged counterparts (Fig. 2).

For the clay loam soil, the soil moisture dry-down curves indicate that biochar significantly increased gravimetric soil water content at permanent wilting point (PWP). The increased water content at PWP in the biochar treatments lead to reduced PAW for both fresh and aged biochar treatments compared to the control (Fig. 1). The results suggest that some water is held in micropores (< 2 nm) or bound too tightly to biochar surfaces to be taken up by plant roots. However, biochar when applied in small amounts (10 g kg^{-1}) has been reported to increase macroporosity (> 50 nm) and PAW in clay soil (Castellini et al., 2015). Among the columns treated with fresh biochars, the columns containing sg.sp biochar had more PAW than the columns with the cs.fp, hw.fp, and sb.fp biochars. Among columns treated with aged biochars, fewer differences were observed but columns with the cs.fp and hw.fp biochars had more PAW then those amended with the sb.fp biochar. Columns amended with fresh cs.fp and hw.fp had less PAW than their aged counterparts while fresh sg.sp columns retained more PAW than columns with aged sg.sp (Fig. 2).

For the sandy loam soil, the soil moisture dry-down curves reveal that fresh biochar increased and aged biochar decreased soil water retention (Fig. 1). This translated to more PAW in the columns containing fresh biochars, regardless of biochar type, compared to the aged biochars (Fig. 2). The increased PAW due to fresh biochar was also higher than the control, while no difference in PAW was found between the aged biochar and control treatments (Fig. 1). Abel et al. (2013) and Hansen et al. (2016) report similar findings for fresh biochars amended to sandy soils; they concluded that biochar increases PAW, which they attribute to greater water held at FC in the biochar treatments. Evaluated by biochar type and within the fresh biochars, cs.sp held the most PAW and hw.sp the least. Among the aged biochars, cs.fp, cs.sp and sg.sp held more PAW than hw.sp (Fig. 2).

The opposing effects of fresh and aged biochars on soil water content and PAW in the sandy loam soil and apparent hydrophobic effect of the aged biochar on water content were unexpected. Our original hypothesis stated that aged biochars would lead to greater improvements in PAW relative to their fresh counterparts; since aged biochars have more oxygen-containing functional groups then fresh biochars (Mukherjee et al., 2014; Bakshi et al., 2016). The WDPT was conducted to provide further insight into this finding (see section 3.2). However, the results of the WDPT did not clarify the trend observed between the sandy loam control and the aged biochar treatments. Further research is needed to explain this apparent hydrophobic effect.

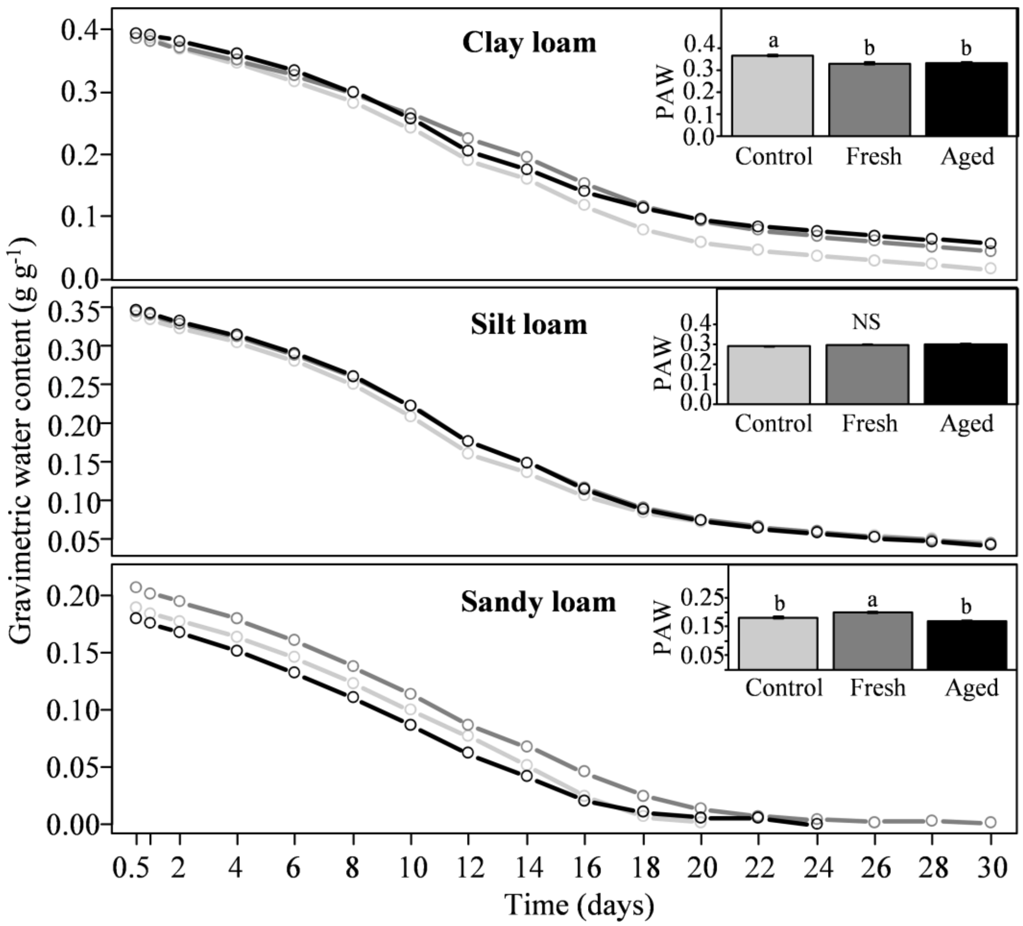

Fig. 1. Effect of fresh and aged biochar on soil water content over time during plant growth within each soil type. Inset bar graphs are the calculated PAW (difference between weight after 24 h (FC) and weight at final weighing) separated by biochar age within each soil type.

Laboratory - Volumetric Soil Water Content and PAW

Significant individual and interaction effects of biochar age, biochar type, and soil type were found on soil water content and PAW as determined by water retention curves (Table 4). For the silt loam soil, biochar and biochar age had no effect on volumetric water content or PAW compared to the control soil (Fig. 3). Differences were found among the aged biochars, as soil with the sb.fp biochar retained more PAW than soil with the hw.fp biochar (Fig.4).

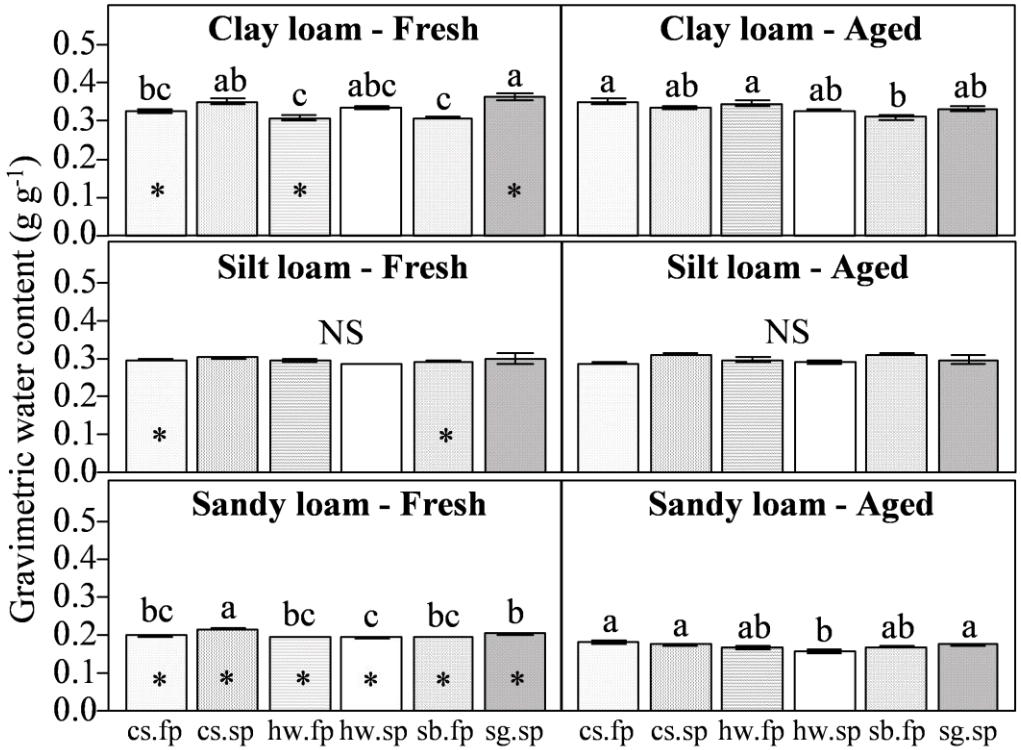

Fig. 2. Effect of biochar type and age on greenhouse PAW within each soil. The fresh biochar bars that contain a star are different than their aged counterparts ($P < 0.05$).

For the clay loam soil, results from the soil water retention curves indicate that at FC the biochar treated soils held less water than the control but held a comparable amount of water at all other matric potentials (Fig. 3). This suggests that the addition of biochar to a poorly drained clay loam soil improves drainage. Moreover, PAW was lower after the addition of both fresh and aged biochar relative to the control, and aged biochar decreased PAW more than fresh biochar (Fig. 3). No differences in PAW were found among the fresh biochars. Soil with the aged cs.fp and hw.fp biochars retained more PAW than soils with the cs.sp and hw.sp biochar treatments. All fresh biochars except for cs.fp and hw.fp retained more PAW than their aged counterparts (Fig. 4).

Our finding that the addition of biochar to a clay loam soil impacts PAW and soil water retention differs from the results of Major et al. (2012) and Hardie et al. (2014) who reported that biochar amended to a clay soil had no significant effect on water holding capacity and no significant effect on PAW or soil retention characteristics, respectively. Further, our results are opposite those reported by Ma et al. (2016) who found enhanced PAW for a clay loam soil following biochar addition, which the authors attribute to increased water retention at FC.

For the sandy loam soil, the water retention curves indicate the same pattern as the soil dry-down curves; with fresh biochar increasing and aged biochar decreasing soil water retention (Fig. 3). Some studies conducted using sandy textured soils agree with our findings that biochar affects soil moisture retention (Gaskin et al., 2007; Abel et al., 2013; Pudasaini et al., 2016), while others report no affect (Hardie et al., 2014; Jeffery et al., 2015). However, the changes in soil water retention resulted in increased PAW only among the fresh biochar treatments compared to the aged biochar treatments, and no differences were found between both fresh and aged biochars relative to the control treatment (Fig. 3). Furthermore, no differences were found between biochar types within both the fresh and aged biochars, but fresh cs.fp, hw.sp, and sb.fp biochars held more PAW than their aged counterparts (Fig. 4).

Overall for the three distinct soils studied, both the soil moisture dry-down curves and the water retention curves indicated similar results for the effect of biochar treatments on soil water retention and PAW. Our findings are largely consistent with the older work of Tryon (1948) who examined the effect of charcoal on soil moisture and found increased available moisture in a sandy soil, no impact in a loamy soil, and decreased available water in a clayey soil. A more recent study by Peake et al. (2014) provides further evidence of the variable influence biochars have on PAW for soils of contrasting textures. The authors examined the effect of three different biochar application rates on the properties of eight diverse soils and found a direct relationship between soil silt content and biochars’ effect on PAW and FC.

Water Use Efficiency

Water use efficiency was affected by soil type, biochar type, and biochar age (Table 4). Within each soil type, the effects of biochar type and age were variable, with no clear pattern apparent. For the silt loam soil, fresh cs.fp and cs.fp biochars increased WUE compared with fresh hw.sp biochar, while aged cs.sp and sb.fp biochars increased WUE relative to cs.fp biochar. Fresh hw.sp and sb.fp biochars decreased WUE compared to their aged counterparts (Fig. 5).

For the clay loam, the soil control had greater WUE compared to all biochar treatments (Table 3). Within fresh biochar treatments, sg.sp biochar had the highest WUE, which was different than cs.fp, hw.fp, and sb.fp biochar treatments. No differences were found between the aged biochars and only fresh cs.fp had decreased WUE relative to its aged counterpart (Fig. 5).

For the sandy loam soil, no differences in WUE were found among the fresh biochars but among the aged biochars, cs.sp had higher WUE than the cs.fp, hw.fp, hw.sp, and sb.fp biochar treatments as well as its fresh counterpart (Fig. 5). Some improvement in WUE in the sandy loam soil is consistent with earlier studies that support increased WUE in maize, quinoa, and tomato crops after biochar application to sandy textured soils (Uzoma et al., 2011; Kammann et al., 2011; Akhtar et al., 2014). Although, the differences we observed were within the aged biochars and not fresh biochars. However, some drainage was observed from the sandy loam soil columns at the final watering event, which did not occur in the other two soils. Although unable to quantify the water lost through drainage, the impact on soil water storage may eliminate differences seen between biochar types within this soil.

Our findings with regards to WUE support the conclusions of Gray et al. (2014) that biochar type, which is influenced by feedstock and pyrolysis conditions in this study, must be considered when producing biochars intended for applications related to water improvement. However, we also show that biochar age is an important variable.

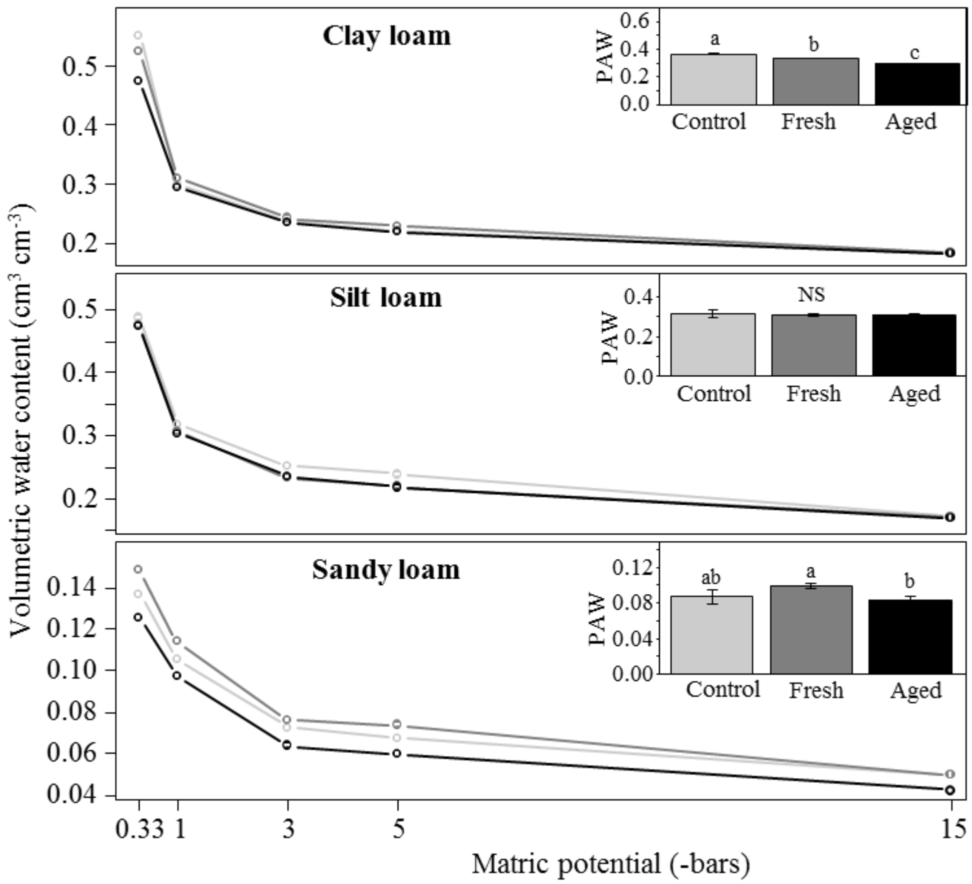

Fig. 3. Water retention curves for biochar age and control treatments within each soil type. Inset bar graphs are the calculated PAW (difference between -0.33 and -15 bars) separated by biochar age within each soil type.

Maize Growth Response

The maximum maize growth stage reached was V5; however, only 45 out of 156 plants reached the V5 stage prior to death. Of these, 38 were from the clay loam soil, seven from the silt loam, and none from the sandy loam soil. The other 111 plants only reached the V4 growth stage prior to death. Final biomass weight was affected by biochar age and biochar type (Table 4).

Biomass weight increased with the addition of fresh biochar in the sandy loam soil and decreased in the clay loam soil relative to both the aged biochar and control treatments (Table 3). For the silt loam soil, fresh biochar increased biomass weight compared to the control but was unchanged relative to aged biochar. Biomass weight was unchanged with the addition of aged biochar relative to the soil control in the clay loam and sandy loam soils, but was increased in the silt loam soil.

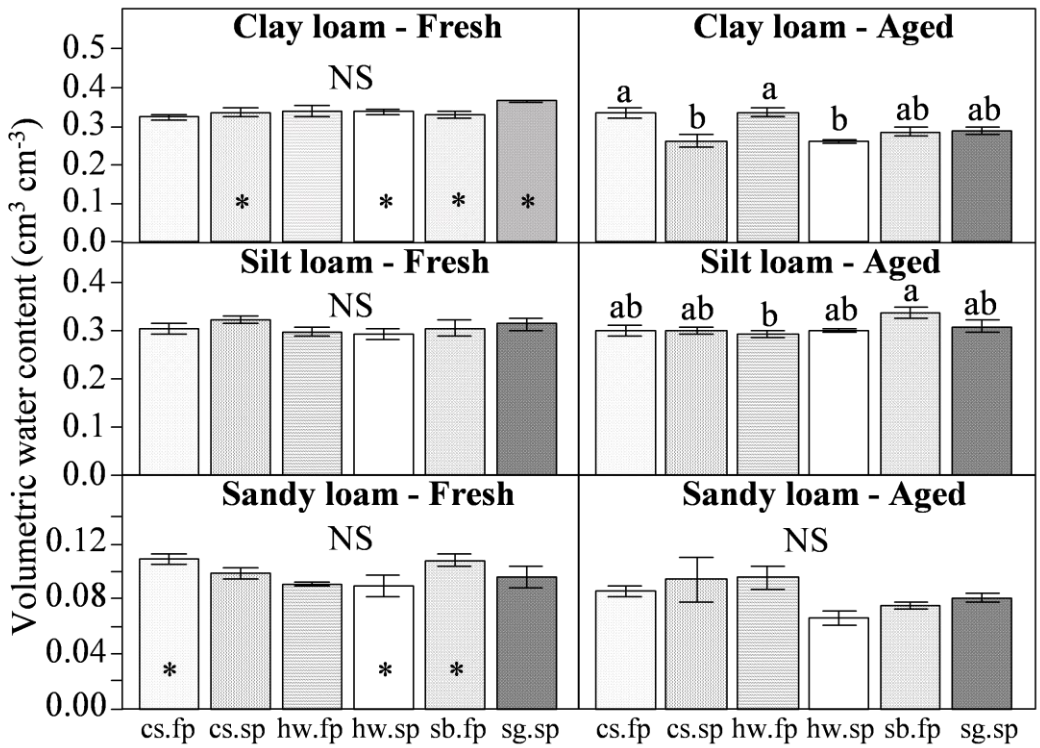

Fig. 4. Effect of biochar type and age on laboratory PAW within each soil. The fresh biochar bars that contain a star are different than their aged counterparts ($P < 0.05$).

When evaluated by biochar type (data not shown), in the silt loam soil cs.sp biochar produced the greatest biomass, which was higher than the hw.sp biochar and control treatments. Biomass for the sb.fp biochar treatment was also greater than the control. For the clay loam, hw.fp and sb.fp biochar treatments had lower biomass than the control. For the sandy loam soil, cs.sp and sg.sp biochars had greater biomass weight than the control and the hw.fp, hw.sp, and sb.fp biochar treatments.

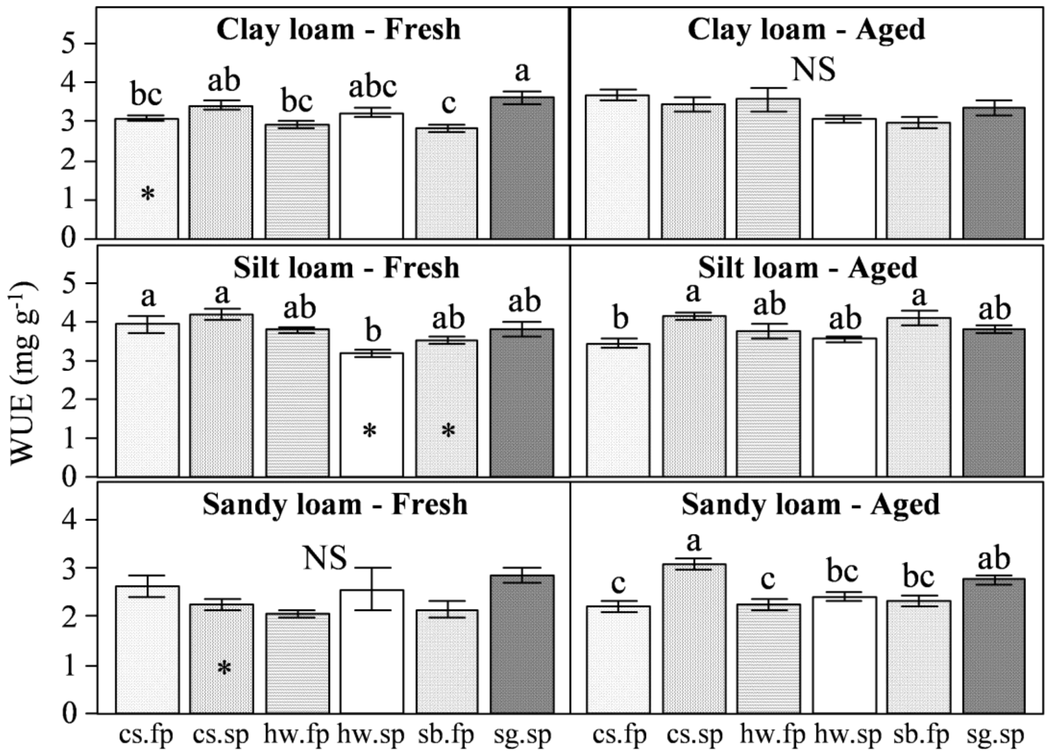

Fig. 5. Effect of biochar type and age on WUE within each soil. For the fresh biochars, bars that contain a star are different than their aged counterparts ($P < 0.05$).

Final plant height was unaffected by biochar type and biochar age; only changing in response to soil type (Table 4). Plants were tallest in the clay loam and shortest in the sandy loam (data not shown). Other studies have reported that the addition of fresh gasification biochar to a sandy loam soil does not increase shoot growth (Hansen et al., 2016) and cowpea biomass is unaffected following the addition of a woody biochar when grown in a loamy sand soil under high water stress (Pudasaini et al., 2016). Maize growth responses measured here were highly variable and were predominantly controlled by soil type.

Conclusions

Biochar has been proposed as a means for positive, lasting improvements for soil water use efficiency and crop growth, however, the results of this study show this is not always true. Aged biochars did not have the same impact on soil-water relations as the equivalent fresh biochars. Results indicated that all laboratory aged biochars were more hydrophilic than their fresh counterparts and the relative degree of biochar hydrophobicity decreased further following a drying-wetting-drying treatment. Furthermore, we found significant interactions effects of soil type, biochar type, and biochar age on WUE and PAW.

Overall, the influence of fresh and aged biochars on the soil and plant properties measured in this study were highly variable and differed by biochar type; resulting in positive, negative, or neutral effects depending on soil type and the response variable being measured. Biochar has a potential role in the global effort to improve water management in rainfed agriculture, but biochar applications must be made strategically. Attention must be given to what biomass feedstock and what pyrolysis conditions are used to produce the biochar, and to what soil is the biochar being applied. Furthermore, our results indicate that results obtained with fresh biochars may not be predictive of long-term effects, because aged biochars may have different impacts on soil water relations than fresh biochars. More research is needed to determine whether results of this relatively short (30 day) greenhouse study are applicable over longer periods of time under field conditions.

Acknowledgements

This project is supported in part by the Global Climate and Energy Project, Stanford Subaward Agreement No. 60413992-112883-A, the National Science Foundation under Grant

Number EPS-1101284, and the USDA-NIFA Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30411. Further support was provided by the Vernon C. Miller Endowed Scholarship and Oblinger Graduate Travel Funds. The authors are also thankful to the anonymous reviewers who helped to improve the quality of this manuscript.

References

Abel, S., Peters, A., Trinks, S., Schonsky, H., Facklam, M., Wessolek, G., 2013. Impact of biochar and hydrochar addition on water retention and water repellency of sandy soil. Geoderma 202-203, 183–191. doi:10.1016/j.geoderma.2013.03.003

Akhtar, S.S., Li, G., Andersen, M.N., Liu, F., 2014. Biochar enhances yield and quality of tomato under reduced irrigation, Agr Water Manage. 138 (31), 37-44, doi.org/10.1016/j.agwat.2014.02.016.

Artiola, J.F., Rasmussen, C., Freitas, R., 2012. Effects of a biochar-amended alkaline soil on the growth of romaine lettuce and bermudagrass. Soil Sci. 177, 561–570. doi:10.1097/SS.0b013e31826ba908

Bakshi, S., Aller, D., Laird, D.A., Chintala, R., 2016. Comparison of the physical and chemical properties of laboratory- and field-aged biochars. J. Environ. Qual. 45, 1627-1634. doi:10.2134/jeq2016.02.0062

Basso, A.S., Miguez, F.E., Laird, D.A., Horton, R., Westgate, M., 2013. Assessing potential of biochar for increasing water-holding capacity of sandy soils. GCB Bioenergy 5 (2), 132–143. doi:10.1111/gcbb.12026

Borchard, N., Siemens, J., Ladd, B., Möller, A., Amelung, W., 2014. Application of biochars to sandy and silty soil failed to increase maize yield under common agricultural practice. Soil Tillage Res. 144, 184-194. doi.org/10.1016/j.still.2014.07.016.

Burrell, L., Zehetner, F., Rampazzo, N., Wimmer, B., Soja, G., 2016. Long-term effects of biochar on soil physical properties. Geoderma 282, 96-102. doi.org/10.1016/j.geoderma.2016.07.019

Castellini, M., Giglio, L., Niedda, M., Palumbo, A.D., Ventrella, D., 2015. Impact of biochar addition on the physical and hydraulic properties of a clay soil. Soil Tillage Res. 154, 1-13. doi.org/10.1016/j.still.2015.06.016.

Das, O., Sarmah, A.K., 2015. Science of the Total Environment The love-hate relationship of pyrolysis biochar and water : A perspective. Sci Total Environ. 1-4. doi:10.1016/j.scitotenv.2015.01.061

Dekker, L.W., Ritsema, C.J., Oostindie, K., Moore, D., Wesseling, J.G., 2009. Methods for determining soil water repellency on field-moist samples. Water Resour. Res. 45 (4), 1-6.

Downie, A., Crosky, A., Munroe, P., 2009. Physical properties of biochar. In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management: Science and Technology. Earthscan, London, UK, pp. 13-32.

Food and Agriculture Organization of the United Nations (FAO), 2003. More crop per drop: the role of agriculture is essential in resolving the world's water problems. http://www.fao.org/english/newsroom/focus/2003/water.htm (accessed 17.01.9)

Food and Agriculture Organization of the United Nations (FAO), 2011. Climate change, water and food security. FAO Water Reports 36. Available from, http://www.fao.org/docrep/014/i2096e/i2096e.pdf

Gaskin, J.W., Speir, A., Morris, L.M., Ogden, L., Harris, K., Lee, D., Das, K.C., 2007. Potential for pyrolysis char to affect soil moisture and nutrient status of a loamy sand soil. In Georgia Water Resources Conference, University of Georgia

Glaser, B., Lehmann, J., Zech, W., 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal-a review. Biol. Fertil. Soils 35, 219-230.

Gray, M., Johnson, M.G., Dragila, M.I., Kleber, M., 2014. Water uptake in biochars: the roles of porosity and hydrophobicity. Biomass Bioenergy 61, 196-205.

Hale, S.E., Hanley, K., Lehmann, J., Zimmerman, A., Cornelissen, G., 2011. Effects of chemical, biological, and physical aging as well as soil addition on the sorption of pyrene to activated carbon and biochar. Environ. Sci. Technol. 45, 10445-10453.

Hansen, V., Hauggaard-nielsen, H., Petersen, C.T., Nørgaard, T., Müller-stöver, D., 2016. Effects of gasification biochar on plant-available water capacity and plant growth in two contrasting soil types. Soil Tillage Res. 161, 1-9. doi:10.1016/j.still.2016.03.002

Hardie, M., Clothier, B., Bound, S., Oliver, G., Close, D., 2014. Does biochar influence soil physical properties and soil water availability? Plant Soil 376, 347-361. doi:10.1007/s11104-013-1980-x

Intergovernmental Panel on Climate Change (IPCC), 2007. Climate Change 2007. Fourth Assessment Report. Cambridge University Press, Cambridge, UK.

International Biochar Initiative (IBI), 2014. Standardized product definition and product testing guidelines for biochar that is used in soil. Report version 2.0 IBI Biochar Standards.

International Water Management Institute (IWMI), 2007. Water for Food, Water for Life. In: Molden, D. (Ed.), A Comprehensive Assessment of Water Management in Agriculture. Earthscan, London, UK.

Jeffery, S., Meinders, M.B.J., Stoof, C.R., Bezemer, T.M., van de Voorde, T.F.J., Mommer, L., van Groenigen, J.W., 2015. Biochar application does not improve the soil hydrological function of a sandy soil. Geoderma 251-252, 47-54. doi:10.1016/j.geoderma.2015.03.022

Kammann, C.I., Linsel, S., Gößling, J.W., Koyro, H.W., 2011. Influence of biochar on drought tolerance of *Chenopodium quinoa* Willd and on soil-plant relations. Plant Soil. 345 (1), 195-210. doi.org/10.1007/s11104-011-0771-5.

Kasozi, G.N., Zimmerman, A., Nkedi-Kizza, P., Gao, B., 2010. Catechol and humic acid sorption onto a range of laboratory-produced black carbons (Biochars). Environ. Sci. Technol. 44, 6189-6195.

Kinney, T.J., Masiello, C.A., Dugan, B., Hockaday, W.C., Dean, M.R., Zygourakis, K., Barnes, R.T., 2012. Hydrologic properties of biochars produced at different temperatures. Biomass Bioenerg. 41, 34-43.

Klute, A., 1986. Water retention: laboratory methods. In: Methods of Soil Analysis, Part 1. 2nd edn (ed. Klute A) pp. 635-662. ASA and SSSA, Madison, WI.

Kuzyakov, Y., Bogomolova, I., Glaser, B., 2014. Biochar stability in soil: decomposition during eight years and transformation as assessed by compound-specific 14C analysis. Soil Biol. Biochem. 70, 229-236.

Laird, D.A., Fleming, P., Davis, D.D., Horton, R., Wang, B., Karlen, D.L., 2010. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. Geoderma 158, 443-449. doi.org/10.1016/j.geoderma.2010.05.013

Lehmann, J., Joseph, S., 2009. Biochar for Environmental Management: Science and Technology. Earthscan, London, UK.

Lim, T.J., Spokas, K.A., Feyereisen, G., Novak, J.M., 2016. Predicting the impact of biochar additions on soil hydraulic properties. Chemosphere 142, 136-144. doi:10.1016/j.chemosphere.2015.06.069

Liu, Z., Demisie, W., Zhang, M., 2013. Simulated degradation of biochar and its potential environmental implications. Environ. Pollut. 179, 146-152.

Ma, N., Zhang, L., Zhang, Y., Yang, L., Yu, C., Yin, G., Doane, T., Wu, Z., Zhu, P., Ma, X., 2016. Biochar improves soil aggregate stability and water availability in a mollisol after three years of field application. PLoS ONE 11(5), e0154091. doi:10.1371/journal.pone.0154091

Major, J., Rondon, M., Molina, D., Riha, S.J., Lehmann J., 2010. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. Plant Soil. 333, 117-128.

Major, J., Rondon, M., Molina, D., Riha, S.J., Lehmann, J., 2012. Nutrient leaching in a Colombian savanna oxisol amended with biochar. J. Envir. Qual. 41, 1076-1086.

Mia, S., Dijkstra, F.A., Singh, B., 2017. Long-term aging of biochar: A molecular understanding with agricultural and environmental implications. Adv. Agron. 141, 1-51. doi.org/10.1016/bs.agron.2016.10.001

Mukherjee, A., Zimmerman, A.R., Hamdan, R., Cooper, W.T., 2014. Physiochemical changes in pyrogenic organic matter (biochar) after 15 months of field aging. Solid Earth 5, 693-704.

Novak, J.M., Lima, I., Xing, B., Gaskin, J., Steiner, C., Das, K., Ahmedna, M., Rehrah, D., Watts, D.W., Busscher, W.J., Schomberg, H., 2009. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. Ann. Environ. Sci. 3, 195-206.

Obia, A., Mulder, J., Martinsen, V., Cornelissen, G., Børresen, T., 2016. In situ effects of biochar on aggregation, water retention and porosity in light-textured tropical soils. Soil Tillage Res. 155, 35-44. doi:10.1016/j.still.2015.08.002

Peake, L.R., Reid, B.J., Tang, X., 2014. Quantifying the influence of biochar on the physical and hydrological properties of dissimilar soils. Geoderma 235-236, 182-190. doi:10.1016/j.geoderma.2014.07.002

Pudasaini, K., Walsh, K.B., Ashwath, N., Bhattarai, T., 2016. Effects of biochar addition on plant available water of a loamy sandy soil and consequences on cowpea growth. Acta Hortic. 1112, 357-364. doi:10.17660/ActaHortic.2016.1112.48

Rajapaksha, A.U., Chen, S.S., Tsang, D.C.W., Zhang, M., Vithanage, M., Mandal, S., Gao, B., Bolan, N.S., Ok, Y.S., 2016. Engineered/designer biochar for contaminant removal/immobilization from soil and water: potential and implication of biochar modification. Chemosphere 148, 276-291.

Rockström, J., Karlberg, L., Wani, S.P., Barron, J., Hatibu, N., Oweis, T., Bruggeman, A., Farahani, J., Qiang, Z., 2010. Managing water in rainfed agriculture-the need for a paradigm shift. Agricultural Water Management Comprehensive Assessment of Water Management in Agriculture 97 (4), 543–550.

Rogovska, N., Laird, D.A., Cruse, R., Fleming, P., Parkin, T., Meek, D., 2011. Impact of biochar on manure carbon stabilization and greenhouse gas emissions. Soil Sci. Soc. Am. J. 75, 871-879. doi:10.2136/sssaj2010.0270

Rogovska, N., Laird, D.A., Rathke, S.J., Karlen, D.L., 2014. Biochar impact on midwestern mollisols and maize nutrient availability. Geoderma 230-231, 340-347. doi.org/10.1016/j.geoderma.2014.04.009

Seredych, M., Bandosz, T.J., 2007. Mechanism of ammonia retention on graphite oxides: role of surface chemistry and structure. J. Phys. Chem. C 111, 15596-15604.

Shi, K., Xie, Y., Qiu, Y., 2015. Natural oxidation of a temperature series of biochars: opposite effect on the sorption of aromatic cationic herbicides. Ecotoxicol. Environ. Saf. 114, 102-108.

Streubel, J.D., Collins, H.P., Garcia-Perez, M., Tarara, J., Granatstein, D., Kruger C.E., 2011. Influence of contrasting biochar types on five soils at increasing rates of application. Soil Sci. Soc. Am. J. 75, 1402-1413

Tryon, E.H., 1948. Effect of charcoal on certain physical, chemical, and biological properties of forest soils. Ecol. Monogr. 18 (1), 81-115.

Uchimiya, M., Chang, S., Klasson, K.T., 2011. Screening biochars for heavy metal retention in soil: Role of oxygen functional groups. J. Hazard. Mater. 190, 432-441.

Uzoma, K.C., Inoue, M., Andry, H., Fujimaki, H., Zahoor, A., Nishihara, E., 2011. Effect of cow manure biochar on maize productivity under sandy soil condition. Soil Use Manage. 27 (2), 205-212.

Verheijen, F., Jeffery, S., Bastos, A.C., van der Velde, M., Diafas, I., 2010. Biochar application to soils: a critical scientific review on effects on soil properties processes and functions. Joint Research Center (JRC), Scientific and Technical Report. Office for the Official Publications of the European Communities, Luxemberg.

Wang, J., Pan, X., Liu, Y., Zhang, X., Xiong, Z., 2012. Effects of biochar amendment in two soils on greenhouse gas emissions and crop production. Plant Soil 360, 287-298.

CHAPTER 5. EVALUATING PEDOTRANSFER FUNCTIONS AND APSIM FOR ESTIMATING BIOCHAR IMPACTS ON SOIL WATER

Modified from a manuscript to be submitted to Agronomy Journal

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Abstract

Accurate estimates of soil water parameters are needed for reliable yield predictions from agricultural crop models. Biochar, a soil amendment, is known to affect soil physical properties such as bulk density and soil water retention. A biochar model was recently developed for the Agricultural Production Systems sIMulator (APSIM) cropping systems model to predict the impacts of biochar on agroecosystems. A modified version of the Saxton and Rawls pedotransfer functions, which include quality modifiers that account for different biochar types, is currently used in the APSIM biochar model to estimate soil water parameters. However, these equations were developed after conducting a literature review and were never tested and validated using experimental data. The objectives of this study were, 1) to compare and evaluate multiple pedotransfer functions for estimating soil water and physical parameters for topsoils with and without biochar and for subsoils without biochar, and 2) to calibrate APSIM biochar parameters and improve accuracy of simulated biochar impacts on soil water property estimates. Forty-eight 1.2 m soil cores were collected from five different soil associations in Iowa. Each core was sectioned into five depth increments and analyzed for organic matter content, texture, and water retention parameters. For topsoils without biochar, the Saxton and Rawls equations were most robust in their estimates of saturation point and drained upper limit, and the Web Soil Survey

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database for estimating the lower limit, bulk density, and plant available water. For topsoils with biochar, the Web Soil Survey database was most robust for estimating all soil water and physical parameters but was not necessarily the most accurate compared to the other soil water equations. Model performance for subsoils was more variable. During biochar model calibration we found that the quality modifiers are site-specific and local calibration is required to accurately predict the impacts of biochar on soil water parameters.

Keywords: APSIM, crop models, biochar, soil organic matter, soil texture, pedotransfer functions

Abbreviations: APSIM, Agricultural Production Systems sIMulator; BD, bulk density; C, carbon; CC, continuous maize; CS, maize-soybean rotation; DUL, drainage upper limit; LL, drainage lower limit; OM, organic matter; PTFs, pedotransfer functions; SAT, saturation point; SOC, soil organic carbon; SWP, soil water parameters; WSS, Web Soil Survey

Introduction

Sophisticated cropping systems models are being increasingly used to investigate complex soil-crop-climate interactions (Jones et al., 2017b; Dietzel et al., 2016). Pedotransfer functions (PTFs) are critical in allowing deployment of such models across regions by relating soil properties such as soil organic matter (SOM) and texture to soil water parameters (SWP), which are necessary for modeling (e.g. Schauberger et al., 2017). However, collecting data on SWP in the field is difficult, time intensive, and costly (Dalgliesh and Foale, 1998; Wösten et al., 2001), thus due to ease and lower costs most soil water measurements are taken in the laboratory and correlated with field estimates (Nemes et al., 2011).

Reliable crop model predictions are dependent on accurate estimates of SWP. However, SWP estimates such as drained upper limit (DUL) are not consistent among different PTFs (Twarakavi et al., 2009; Nemes et al., 2011). Discrepancies in estimates of SWP between studies and PTFs occur because values are determined using a single matric potential, which may be insufficient for accurately predicting SWP due to differences in soil properties such as texture, bulk density (BD), and salinity (Gijsman et al., 2003). Gijsman et al. (2003) found errors and inconsistencies in SWP estimated using eight different PTFs. Further, other studies have attempted to generate correction factors for previously estimated DUL values to improve their accuracy (Nemes et al., 2011). Recently, Palmer et al. (2017) developed an 'ensemble PTF' to estimate DUL and the lower limit (LL) by using the arithmetic mean of estimates from several established PTFs. This was done because different PTFs were developed using different methodologies and datasets from a range of environments. Thus, the ensemble equations take into account soil textural class when estimating SWP at different matric potentials (Palmer et al., 2017).

In addition to the method selected to estimate SWP, the soil properties included in PTFs are important. For example, the effect of soil texture on soil water retention has been known and considered to be an important parameter in models since the early 1900's (Briggs and Shantz, 1912). However, not until more recently was SOM included as an input parameter in models (Gupta and Larson, 1979; Rawls et al., 1982) and its impact on soil water retention fully appreciated (Hudson, 1994). As a result, early modeling work emphasized the effects of soil texture on soil water retention but largely ignored or downplayed SOM impacts on SWP estimates (Olness and Archer, 2005). Now the importance of SOM on SWP is widely recognized, however, the accuracy of PTFs that use both SOM and texture as inputs for estimating SWP are still being investigated. Moreover, estimates of DUL and LL from some models (e.g., APSIM and Daycent) remain constant over time because they are not linked to changes in SOM. It is critical that models take into account the impacts of SOM on SWP estimates and consider management practices, such as biochar amendments, that may impact SOM and SWP.

Biochar, the solid co-product of biomass pyrolysis, is intended for soil application to improve soil quality while sequestering carbon (Lehmann et al., 2006; Laird, 2008; Woolf et al., 2010; Laird et al., 2017). Biochar is physically and chemically a very diverse material. It is inherently different from other forms of SOM because it may be stable in soils for hundreds to thousands of years (Lehmann et al., 2009). Biochars generally have high porosity and large surface areas, which affect soil water and physical properties including BD, hydraulic conductivity, pore size distribution, and water retention (Gaskin et al., 2007; Atkinson et al., 2010; Zwieten et al., 2012; Basso et al., 2013; Akhtar et al., 2014; Hardie et al., 2014). These properties, however, may change as biochars weather or age in soils, hence the potential impacts of biochar on soil properties and crop yields are uncertain and changing (Cheng and Lehmann, 2009; Tammeorg et al., 2016; Mia et al., 2017). Biochars impact on agronomic and environmental systems further depends on: rate of application, biomass feedstock, and pyrolysis conditions (Verheijen et al., 2010; Ippolito et al., 2012). A recently developed biochar model (Archontoulis et al., 2016) within the Agricultural Production Systems sIMulator (APSIM) cropping systems model (Holzworth et al., 2014), for the first time integrates these complex variables to provide a systems level understanding of biochars impact on agro-environmental systems, including biochar effects on SWP. However, as with all models, the biochar model must be properly calibrated and validated before widespread use in diverse environments.

During APSIM biochar model development the PTFs of Saxton and Rawls (2006) were selected for use because both soil texture and SOM information were considered and the PTFs were developed using multiple datasets (USDA/NRCS National Soil Characterization database (Soil Survey Staff, 2004)). Archontoulis et al. (2016) modified the Saxton and Rawls (2006) soil water equations to predict the rate of change in DUL and LL over time. Moreover, they estimated the rate of change in BD and saturation point (SAT) by combining the Saxton and Rawls (2006) PTFs with an equation developed by Andales et al. (2000), which accounts for tillage and precipitation effects on BD. These modified rate equations were coupled with a set of quality modifiers to account for different biochar types (Archontoulis et al., 2016).

Model predictions using the modified rate PTFs were found reasonable based on a qualitative assessment of the biochar literature, i.e., biochar additions have a larger effect on low OM soils compared to high OM soils and different types of biochar have larger or smaller effects on soil hydrology (Laird et al., 2010; Liu et al., 2012; Basso et al., 2013; Cornelissen et al., 2013; Herath et al., 2013; Gai et al., 2014; Lim et al., 2016**)**. However, model simulations of biochar impacts on SWP were never tested using experimental data and the accuracy of the PTFs used for estimating SWP across a range of soil types was never quantified. Additionally, the quality modifiers and their initial values were selected based on the literature available during model development but were also never tested against experimental measurements. Finally, the PTFs of Saxton and Rawls (2006) and others were not developed using nor tested in biochar amended soils, thus do not take into account the inherent differences between biochar and biogenic SOM. Consequently, the validity of the soil water equations of Saxton and Rawls (2006) and other

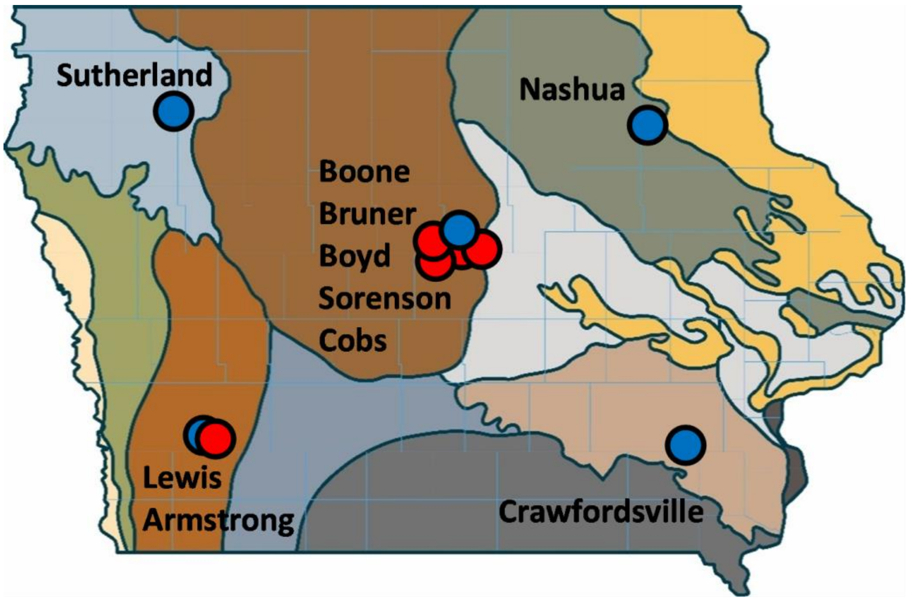
PTFs (Gijsman et al., 2003: Palmer et al., 2017) for soils amended with biochar is unknown. This study aims to fill these knowledge gaps because accurate estimates of SWP for biochar amended soils are needed to improve overall model predictions of biochar impacts on agro-ecosystem functions.

Our specific objectives were to 1) compare and evaluate the prediction accuracy of different PTFs for estimating SWP of topsoils with and without biochar (N = 146) and subsoils without biochar (N =80) from new experimental data, 2) quantify the accuracy of the APSIM biochar model before and after calibration for estimating biochar impacts on soil hydrology and determine whether generalized or site-specific parameter values are needed for modeling. We hypothesize that SWP estimates will differ for soils with and without biochar because biochar is qualitatively different than biogenic SOM. We further hypothesize that model performance will improve after making site-specific adjustments to the biochar quality modifiers.

Materials and Methods

Soil Sample Collection

In fall 2015, 40 soil cores were collected from ten different field sites located in five different soil association regions of Iowa (Fig. 1). An additional eight soil cores were collected in summer 2016. All cores were collected using a hydraulic probe to a depth of 1.2 m (Giddings Machine Co., Windsor, Co, USA) and were refrigerated until analyzed. Collected samples differed by soil series, the presence or absence of biochar, biochar application rate, and biochar age (i.e. time since application). Site management varied little between locations (Fig. 1).



Site	Latitude, Longitude	Cropping system*	Dominant soil series
Boone	42.02, -93.77	CC	Clarion
Bruner	42.00, -93.73	CC	Nicollet
Boyd	42.00, -93.79	CC	Clarion
Lewis	41.31, -95.17	CC	Exira
Sorenson	42.00, -93.74	CC and CS and C-C-C/SG-SG-SG-SG	Webster and Clarion
Cobs	41.91, -93.75	CS	Nicollet and Webster
Armstrong	41.18, -95.10	CS	Marshall
Nashua	42.93, -92.57	CS	Readlyn and Kenyon
Crawfordsville	41.19, -91.48	CS	Kalona
Sutherland	42.92, -95.54	CS	Marcus and Sac

* CC- continuous maize, CS- maize soybean rotation, SG- switchgrass

Fig. 1. Geographic location of the ten sampling sites used in this study. Different background colors indicate major soil associations of Iowa. Red circles indicate sites with and without biochar applications. Blue circles indicate sites with no biochar applications.

Database Development and Laboratory Analyses

The 48 soil cores were sectioned into five depth increments (0-5, 5-15, 15-30, 30-50, 50-90 cm) generating a total of 226 samples[1]. A subsample of intact soil was collected from each depth increment using a metal ring with dimensions 3.8 cm high and 5.3 cm in diameter. The

[1] subsoil data from seven cores was not collected

total number of samples representing soil from the top three depth increments (topsoil), was N = 146 soil rings (85 with biochar and 61 without biochar). Subsoil samples were collected from the >30-90 cm depth increments and contained no biochar (N = 80). The soil samples were texturally diverse, ranging from sandy loam to silty clay loam (Fig. 2).

All soil samples were analyzed for saturation point, water retention at -0.33, -1, -3, -5, -15 bar, bulk density (g cm^{-3}), texture, and SOM content. The intact soil core subsamples were saturated from the bottom up with a 0.005 M $CaCl_2$ solution for 24 h and then weighed to determine the wet weight of the sample at the saturation point. The pressure plate method was then used to determine water held at matric potentials of -0.33, -1, -3, -5, and -15 bar (Klute, 1986) using a Ceramic Plate Extractor (Soil Moisture Equipment Corp., Santa Barbara, CA, USA). The -0.33 and -1 bar measurements were conducted using the intact soil cores. The cores were placed on ceramic plates inside the pressure chamber. Pressure inside the chamber was held constant until water stopped draining, at which time the samples were weighed. Following data collection for water retained at -1 bar, a subsample of the core soil was weighed, dried overnight at 105 °C and weighed again. The oven dry weights were used to determine bulk density and moisture content at saturation, -0.33 bar, and -1 bar. The remainder of the soil core subsample was sieved to <2 mm, repacked into 1 cm high by 3 cm diameter rubber rings, saturated as previously described, and analyzed for water held at matric potentials of -3, -5, and -15 bar. After samples had reached equilibrium and been weighed at each of these matric potentials, the samples were dried overnight at 105 °C and reweighed. Plant available water content (PAW) was determined by the difference in volumetric water content between -0.33 (DUL) and -15 bar (LL) moisture content.

Organic matter content was determined for each soil using the Loss on Ignition method (Nelson and Sommers, 1996). A 2-3 g soil sample (sieved <2 mm) was initially weighed into a pre-weighed ceramic crucible, oven dried at 105 °C overnight, and reweighed. Samples were subsequently placed in a muffle furnace (Thermo Scientific Lindberg/Blue M Box Furnace BF51894C-1) set to 400 °C for 12 h. Samples were removed from the furnace after 12 h, cooled in a desiccator, and weighed again. Percent OM was determined as the difference in sample weight determined after the 105 °C treatment and sample weight determined after the 400 °C treatment divided by the 105 °C sample weight multiplied by 100. Percent organic carbon (OC) in the soil samples was estimated by dividing %OM values by 1.72, a widely used conversion factor (Nelson and Sommers, 1982).

Particle size analysis was determined with the hydrometer method (Gee and Bauder, 1986). Approximately 20 g of air-dry soil (sieved <2 mm) was weighed into 600 mL plastic beakers, 250 mL distilled water and 50 mL of 5% sodium-hexametaphosphate solution were added to each beaker and left to soak overnight. Subsequently, a sonicator (model no. FB505 Fischer Scientific) was used to disperse soil particles. Each sample was sonicated with the probe tip at 2.5 cm below the water’s surface for two minutes at an amplitude of 50% and pulse duration of 59 seconds with a one second rest between pulses. After sonication samples were quantitatively transferred to 1000 mL graduated cylinders and made up to volume with distilled water. Samples were agitated by means of a rubber stopper fixed to the end of a pole for 30 s immediately prior to the analysis (to set time zero). Hydrometer readings were taken after 30 s, 60 s, 90 mins, and 24 h. Temperature of the blank suspension was measured at the same time intervals as the hydrometer readings. All reported values were corrected against a blank suspension of 50 mL of 5% sodium-hexametaphosphate solution and distilled water made up to 1000 mL as well as the measured moisture content of each soil sample.

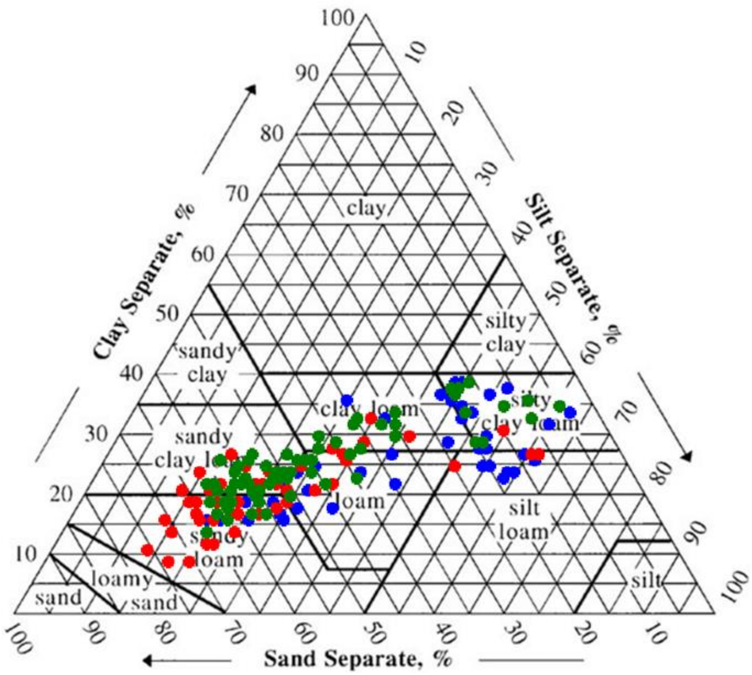


Fig. 2. Textural distribution of all 226 soil samples collected from the nine field sites. Blue circles indicate soils without biochar (N = 61) and red circles indicate soils with biochar (N = 85) from the topsoil (0-5, 5-15, and 15-30 cm depth increments). Green circles indicate subsoil samples (N = 80) that contain no biochar (30-50 and 50-90 cm depth increments).

Pedotransfer Function Evaluation

The soil water and physical parameters estimated using PTFs developed by Gijsman et al. (2003), Saxton and Rawls (2006), and Palmer et al. (2017), and parameters for the corresponding soil series, obtained from the Web Soil Survey (WSS) database, were compared with laboratory measured soil water and physical parameters to assess the accuracy of the PTFs and their applicability for estimating parameters of biochar amended soils. The equations and details of the PTFs evaluated are provided in the supplemental materials (Table S1). We evaluated estimates of bulk density (BD), drained upper limit (DUL), lower limit (LL), saturation point (SAT), and plant available water (PAW). Because the WSS database does not include values for SAT, we estimated SAT from the WSS BD values using equation (1) below.

$$SAT = 1 - \frac{BD}{2.65} \qquad \text{Eq. (1)}$$

Model Set-up, Description, and Calibration

We used APSIM version 7.9 (Holzworth et al., 2014) and plugged in the following models: maize and soybean crop models (Keating et al., 2003), Soil N (soil N and C cycling model with the default soil temperature model; Probert et al., 1998), SoilWat (a tipping bucket soil water model; Probert et al., 1998); SURFACEOM (a crop residue model; Probert et al., 1998; Thorburn et al., 2001, 2005); the biochar model (Archontoulis et al., 2016), and the following management activities: planting, harvesting, tillage, fertilizer (Keating et al., 2003).

Meteorological data for each site came from the Iowa Environmental Mesonet (2017). Data collected from each soil depth increment were used to create soil profiles for each site in APSIM similar to Archontoulis et al. (2014a). The multiple PTFs were evaluated separately for topsoils (0-30 cm) with and without biochar and subsoils (>30-90 cm). Only the topsoils were used during biochar model calibration because 30 cm represents the maximum depth of biochar incorporation at any site. Initial SOM profile values were adjusted slightly if necessary at the start of the simulation (2005) to match the 2016 measured SOM values. Additional soil parameters required to run the model, such as evaporation, runoff, and drainage parameters were calculated as described by Archontoulis et al. (2014a). Other inputs included measured data and default parameter values for: BD, DUL, LL, SAT, texture and % OC. All simulations were run from 2005 to 2016 using local cultivars and known management (Archontoulis et al., 2014 a, b;

Archontoulis and Licht, 2016; Basche et al., 2016; Dietzel et al., 2016; Martinez-Feria et al., 2016; Puntel et al., 2016).

The APSIM biochar model uses the following set of equations to relate changes in biochar and soil organic carbon (SOC) to changes in hydrological parameters on a daily basis (Archontoulis et al., 2016):

$$\Delta DUL = Q_{DUL} \times (0.0261 + 0.0072 \times sand - 0.0561 \times clay) \times \Delta SOC \qquad \text{Eq. (2)}$$

$$\Delta BD = Q_{BD} \times (-0.2332 + 0.115 \times sand + 0.35 \times clay) \times \Delta SOC \qquad \text{Eq. (3)}$$

$$\Delta LL = Q_{LL} \times (0.0118 + 0.0098 \times sand - 0.0255 \times clay) \times \Delta SOC \qquad \text{Eq. (4)}$$

where ΔDUL is the daily rate of change in the DUL, ΔBD is the daily rate of change in BD, ΔLL is the daily rate of change in the LL, ΔSOC is the daily rate of change in SOC (ΔSOC also includes biochar C), and sand and clay are the percent sand and percent clay, respectively. Equations 2-4 were derived from the Saxton and Rawls (2006) equations. The Q_{DUL}, Q_{BD}, and Q_{LL} are empirical modifiers (Equations 5-7 and Fig. 3) incorporated into the biochar model to account for different biochar types:

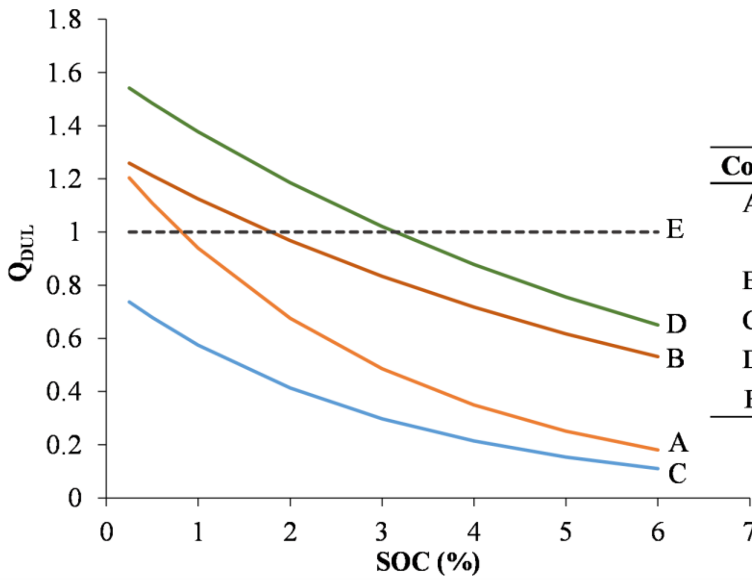
$$Q_{DUL} = \alpha * e^{(-K_{DUL} \times SOC)} \qquad \text{Eq. (5)}$$

$$Q_{BD} = \alpha * e^{(-K_{BD} \times SOC)} \qquad \text{Eq. (6)}$$

$$Q_{LL} = e^{(-K_{LL} \times SOC)} \qquad \text{Eq. (7)}$$

where K_{DUL}, K_{BD}, and K_{LL} are empirical slope coefficients and α is a constant value (default of 1.3067). When K_{LL}, K_{DUL}, and K_{BD} are set to 1, 0, and 0, respectively, the biochar quality modifiers are cancelled, and equations 2-4 default to the original Saxton and Rawls (2006) equations.

A graphic illustrating the effect of SOC on the biochar quality DUL modifier is provided below (Fig. 3).



Code	Parameter values
A	default APSIM biochar model α=1.3067, K_{DUL}=0.33
B	α=1.3067, K_{DUL}=0.15
C	α=0.8, K_{DUL}=0.33
D	α=1.6, K_{DUL}=0.15
E	α=1, K_{DUL}=0

Fig. 3. Impact of SOC and the intercept (α) and slope (K_{DUL}) values in the biochar quality DUL modifier equation on Q_{DUL} values.

The daily rate of change in BD is influenced by a second equation that accounts for tillage effects (equation 14 in Archontoulis et al., 2016) and the new ΔBD value is the minimum of the calculated effect of biochar on BD and the effect of tillage on BD. In the default APSIM 7.9 version of the biochar model, biochar impacts on DUL and BD (and therefore SAT) are considered, while biochar effects on LL were set to zero because of inconsistent findings for biochars effect on LL in the literature during model development (Brockhoff et al., 2010; Laird et al., 2010; Liu et al., 2012; Basso et al., 2013; Cornelissen et al., 2013; Herath et al., 2013; Archontoulis et al., 2016).

During model set-up for the plots with biochar (Fig. 1), we incorporated site specific variables such as date of biochar application, amount of biochar applied, depth of biochar incorporation, fraction of C in biochar, biochar C:N ratio, and soil sand and clay contents into the model (Table S2). Biochar parameter values such as priming effects, K_{DUL}, decomposition rates, etc. were left at the default values determined by Archontoulis et al. (2016). During model calibration adjustments were made to the following variables to improve model performance: biochar fraction lost at time of application (f_{loss}), K_{DUL}, K_{BD}, and the intercept parameter α in both the Q_{DUL} and Q_{BD} equations.

Statistical Analysis

The goodness of fit between measured and estimated values were assessed by calculating the root mean square error (RMSE) and mean absolute error (MAE) as defined in Archontoulis and Miguez (2015). We also used the slope and R^2 values for measured versus predicted fitted regression equations (intercept forced to zero; y = slope*X) as additional measures of model performance. An analysis of covariance (ANCOVA) was performed in R (version 3.3.1) to compare regression line parameter values (slope and intercept) used to evaluate the relationship between PAW and SOM from measured and predicted data. Statistical significance was assessed at the 5% alpha level. Performance of both the uncalibrated and calibrated APSIM biochar model and the original Saxton and Rawls (2006) equations were evaluated by calculating the RMSE, relative root mean square error (RRMSE), and modeling efficiency (ME). We used the rating scale described by Ma et al. (2011) for agricultural models, which rates model performance as very good, good, and satisfactory when the RRMSE <10%, 10-15%, and 15-20%, respectively.

Modeling efficiency assesses predictive capacity on a scale of <0 to 1, higher ME values are better.

Results

Pedotransfer Function Evaluation for Topsoils with and without Biochar

Soil water and physical parameters (SAT, DUL, LL, BD, and PAW) from the WSS database and as predicted using multiple PTFs were compared with measured parameters for topsoils with and without biochar. For topsoils without biochar, all of the studied methods for estimating soil water and physical parameters yielded results in general agreement with the measured values, except for estimates of LL using the PTF of Gijsman et al. (2003), which performed significantly different and worse than the other methods (Table 1). Specifically, based on model robustness (slope) the PTFs of Saxton and Rawls (2006) provided the best estimates for SAT, and DUL, while the WSS database provided the best estimates of LL, BD, and PAW relative to the measured data. In terms of model error (RMSE and MAE) the Saxton and Rawls (2006) PTFs had the lowest error for all SWP estimates except for PAW which was best estimated by the WSS database. Results differed for soils with biochar (Table 1). WSS yielded the most accurate estimates for all SWP based on model robustness, but only had the lowest modeling error for estimates of SAT, DUL, and PAW. The PTFs of Saxton and Rawls (2006) resulted in less error for estimates of LL and BD (Table 1).

Table 1. Performance of the Web Soil Survey (WSS) database and established PTFs of Saxton and Rawls (2006) (S&R), Gijsman et al. (2003)* (Gijsman), and Palmer et al. (2017)† (Palmer) for estimating soil water and physical parameters for soils with and without biochar between 0-30 cm depth. The slope was determined from a y=a*x regression with the intercept forced to zero, RMSE has units mm mm^{-1} for SAT, DUL, LL, PAW and g cm^{-3} for BD, and MAE is unitless.

Parameter	*Slope*				*RMSE*				*MAE*			
	WSS	**S&R**	**Gijsman**	**Palmer**	**WSS**	**S&R**	**Gijsman**	**Palmer**	**WSS**	**S&R**	**Gijsman**	**Palmer**
Soils WITHOUT biochar												
SAT	0.854	0.867	0.815	0.815	0.107	0.089	0.118	0.118	0.088	0.078	0.112	0.112
DUL	0.850	0.895	1.123	0.763	0.069	0.057	0.069	0.100	0.056	0.047	0.058	0.088
LL	1.00	0.955	19.771	0.753	0.042	0.028	3.549	0.061	0.032	0.022	3.549	0.051
BD	0.985	0.979	1.566	0.814	0.193	0.097	0.748	0.264	0.156	0.079	0.739	0.227
PAW	1.105	0.819	0.603	0.764	0.042	0.044	0.074	0.052	0.034	0.037	0.068	0.043
Soils WITH biochar												
SAT	0.879	0.846	0.831	0.831	0.085	0.099	0.108	0.108	0.072	0.089	0.098	0.098
DUL	0.899	0.843	1.257	0.685	0.053	0.061	0.096	0.109	0.043	0.051	0.088	0.102
LL	0.986	0.975	23.504	0.631	0.023	0.020	3.554	0.066	0.019	0.015	3.554	0.060
BD	0.986	1.032	1.578	0.815	0.121	0.089	0.757	0.253	0.099	0.072	0.751	0.230
PAW	1.202	0.705	0.637	0.727	0.052	0.056	0.065	0.053	0.045	0.049	0.057	0.045

* Gijsman et al. (2003) adapted the PTFs to estimate SAT and LL from Rawls et al., (2003) and Ritchie et al., (1986), respectively.
† Palmer et al. (2017) adapted the PTFs to estimates BD and SAT from Adams (1973) and Dalgliesh and Foale (1998), respectively.

The efficacy of the Saxton and Rawls (2006) PTFs as currently used in the APSIM biochar model 7.9 is illustrated in Figure 4 for all 0-30 cm soil samples. The performance of the other PTFs and the WSS database are presented in the supplemental materials (Figs. S1-S3). On average, the Saxton and Rawls (2006) PTFs underestimated all soil water and physical parameters compared to the measured values (slopes in Figure 4). The greatest agreement between measured and predicted values were for estimates of LL and BD. Underestimation of DUL caused a substantial underestimation of PAW, which is calculated as the difference between DUL and LL (Fig. 4). The slopes of the measured versus predicted PAW regression lines are 0.8194 and 0.7047 for the no-biochar and biochar soils, respectively. This suggests that the PTFs (without any quality modifiers) are underestimating PAW by 18 and 30% for the no-biochar and biochar soils, respectively.

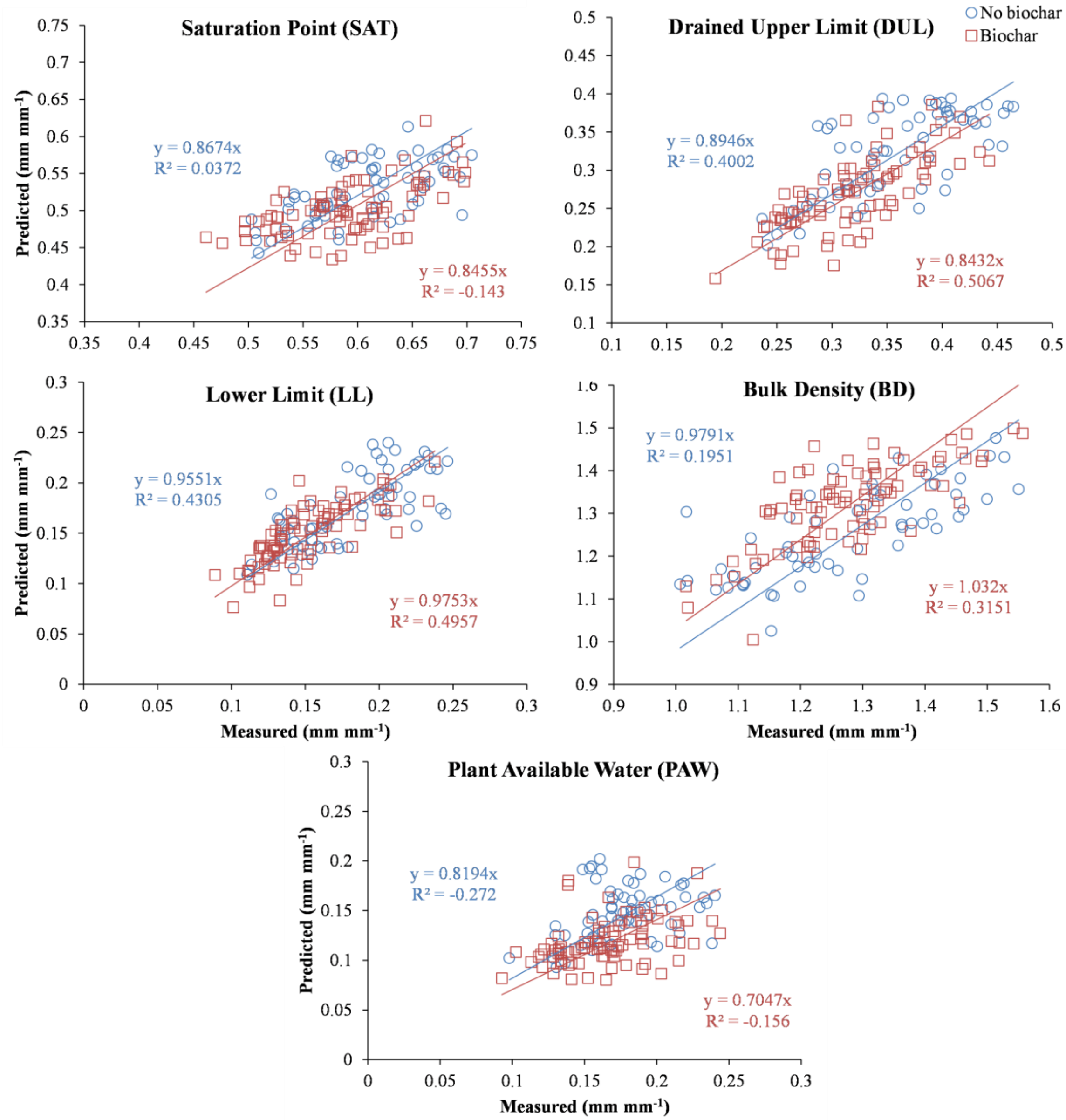


Fig. 4. Measured versus predicted soil water and physical parameter values estimated using the Saxton and Rawls (2006) PTFs for topsoils with biochar (N=85) and without biochar (N=61).

The relationship between measured SOM and measured PAW is shown in Figure 5. The rate of increase (see slopes in Fig. 5) for soils with and without biochar, which is the foundation in the current APSIM biochar model, were similar. The predicted SOM vs. PAW relationship from the Saxton and Rawls (2006) PTFs had slopes of 0.0141 for the soils with biochar and 0.0125 for the soils without biochar (data not shown). The Saxton and Rawls (2006) PTFs underestimated PAW for a given SOM content for both soils with and without biochar compared to measured data. However, the similarity between the slopes suggests that the equations correctly predict the relationship between these two variables. Furthermore, no significant differences were found between the slopes of the PAW vs SOM relationship for measured ($P = 0.427$) and predicted ($P = 0.596$) data for both the biochar and no-biochar soils (data not shown). However, a significant difference was found between the intercept values for the PAW vs SOM relationship for the soils with and without biochar in both the measured ($P = 0.04$) and predicted ($P < 0.0001$) data. The similarity between the slope values for the measured data, predicted data, and after comparing the measured and predicted data for both biochar and no-biochar soils indicates that no differences exist in the rate of change between biochar C and biogenic OM in these soils when estimating PAW using the Saxton and Rawls (2006) PTFs. However, the differences between intercept values indicate that differences exist in the magnitude of change in PAW estimates for a given SOM content for soils with and without biochar, confirming that the Saxton and Rawls (2006) PTFs underestimate PAW compared to measured values. Thus, we further evaluated the impacts biochar has on SWP estimates using the modified Saxton and Rawls (2006) PTFs in the APSIM biochar model.

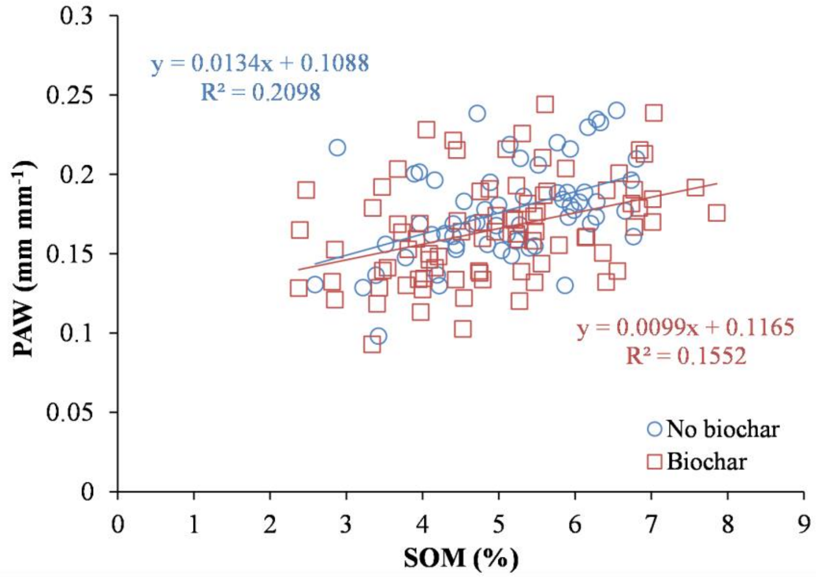


Fig. 5. Measured estimates illustrating the relationship between plant available water and soil organic matter for topsoils with biochar (N = 85) and without biochar (N = 61).

Pedotransfer Function Evaluation for Subsoils without Biochar

Similar to the results for topsoils with and without biochar, all of the PTFs evaluated yielded results in general agreement with the measured values for subsoils, except for the estimate of LL using the PTF of Gijsman et al. (2003), which again performed poorly compared to the other methods (Table 2). Specifically, based on model robustness and error, the PTFs of Gijsman et al. (2003) and Palmer et al. (2017) performed equally well for estimating SAT, the PTFs of Saxton and Rawls (2006) provided the best estimates for DUL and LL, and the WSS database was best for estimating PAW relative to the measured data. For estimates of BD, the WSS database was most robust, but the Saxton and Rawls (2006) PTFs had less error (Table 2).

Table 2. Performance of the Web Soil Survey (WSS) database and established PTFs of Saxton and Rawls (2006) (S&R), Gijsman et al. (2003)* (Gijsman), and Palmer et al. (2017)† (Palmer) for estimating soil water and physical parameters for subsoils >30-90 cm depth. The slope was determined from a y=a*x regression with the intercept forced to zero, RMSE has units mm mm^{-1} for SAT, DUL, LL, PAW and g cm^{-3} for BD, and MAE is unitless.

Parameter	*Slope*				*RMSE*				*MAE*			
	WSS	**S&R**	**Gijsman**	**Palmer**	**WSS**	**S&R**	**Gijsman**	**Palmer**	**WSS**	**S&R**	**Gijsman**	**Palmer**
SAT	0.795	0.788	0.817	0.817	0.130	0.132	0.120	0.120	0.118	0.122	0.106	0.106
DUL	0.892	0.909	1.099	0.673	0.046	0.044	0.052	0.112	0.039	0.024	0.044	0.105
LL	0.957	1.064	23.59	0.731	0.029	0.025	3.577	0.051	0.023	0.016	3.577	0.043
BD	1.067	1.079	1.544	0.817	0.160	0.140	0.739	0.268	0.130	0.091	0.729	0.239
PAW	1.082	0.744	0.651	0.608	0.032	0.049	0.060	0.069	0.027	0.032	0.055	0.063

* Gijsman et al. (2003) adapted the PTFs to estimate SAT and LL from Rawls et al., (2003) and Ritchie et al., (1986), respectively.
† Palmer et al. (2017) adapted the PTFs to estimates BD and SAT from Adams (1973) and Dalgliesh and Foale (1998), respectively.

The performance of the Saxton and Rawls (2006) PTFs for estimating soil water and physical parameters in subsoils and the relationship between SOM and PAW from both measured and predicted estimates are illustrated in Figures 6 and 7, respectively. The performance of the other PTFs and the WSS database are presented in the supplemental materials (Figs. S4-S6).

The Saxton and Rawls (2006) PTFs performed quite well for estimating DUL, LL, and BD but underestimated SAT and PAW in these subsoils (Fig. 6). Similar to the results found for the topsoils with and without biochar, the Saxton and Rawls (2006) PTFs underestimated PAW for a given SOM content in subsoils compared to measured data (Fig. 7). The difference between measured and predicted estimates in describing the relationship between SOM and PAW was significant ($P = 0.02$). Specifically, both the rate of change ($P = 0.02$) and the magnitude of the difference ($P = <0.0001$) were different between measured and predicted estimates. This indicates that the Saxton and Rawls (2006) PTFs are underestimating PAW for a given SOM content and are not accurately depicting the relationship between PAW and SOM in the subsoils analyzed.

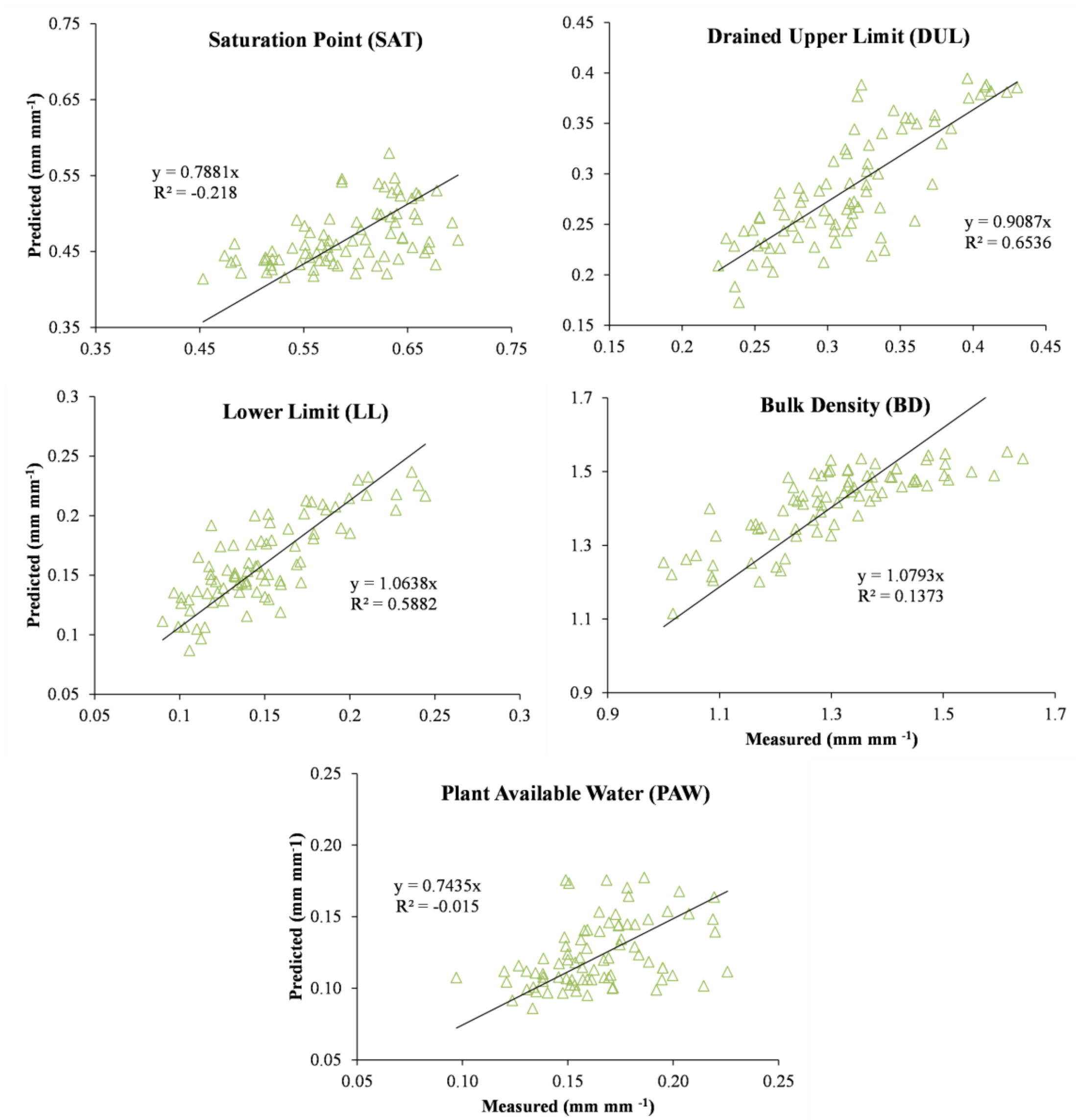


Fig. 6. Measured versus predicted soil water and physical parameter values estimated using the Saxton and Rawls (2006) PTFs for subsoils (N = 80).

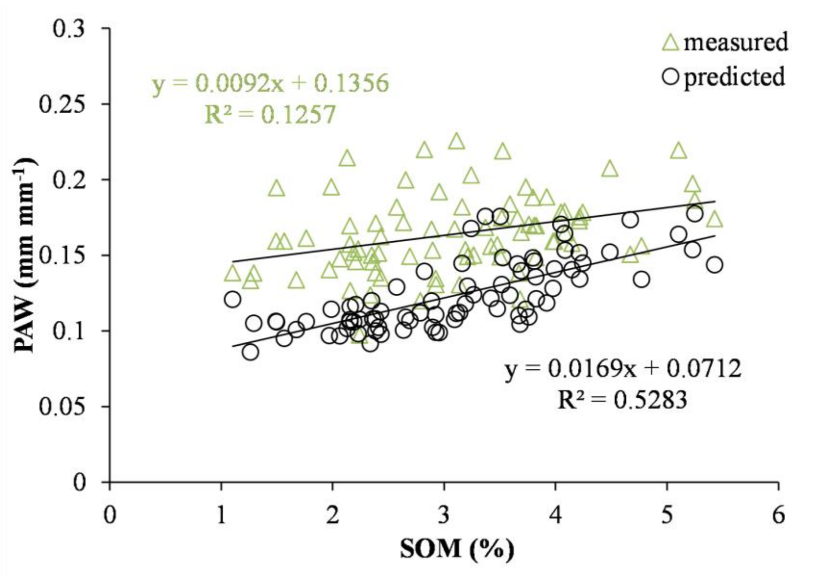


Fig. 7. Measured and predicted estimates of the relationship between plant available water and soil organic matter for subsoils (N = 80).

APSIM Biochar Model Calibration

Changes to the DUL and BD quality modifiers (i.e. the intercept and slope parameters within the Q_{DUL} and Q_{BD} equations) were determined to be site specific as different values led to improved model performance at different sites (Table 3; Fig 1). For example, at the Sorenson site the intercept values for DUL and BD were increased to 3.23 and 2.55, respectively, from the default value of 1.3 because the uncalibrated model underestimated biochars impact on these SWP. By increasing the intercept value, the initial estimates of DUL and BD were in better agreement with the measured values. Further, the values for the slope parameters, K_{DUL} and K_{BD}, were decreased from the default value of 0.33 to 0.1 and 0.05, respectively, so that the rate of change in the final estimates of DUL and BD were smaller (Table 3). Different values for the slope and intercept in the DUL and BD quality modifiers were needed for the Boone site than for the Sorenson site. For the Boone site, the default value was used for the intercept value and the slope values were increased to 1 for both DUL and BD (Table 3).

Table 3. Properties of the biochars applied at the field sites, input biochar parameter values used during model set-up and calibration, and calibrated parameter values.

Parameter	Value (Boone)	Value (Bruner)	Value (Boyd)	Value (Lewis)	Value (Sorenson)
Biochar properties					
Source	Royal Oak Charcoal	Royal Oak Charcoal	ICM, Inc.	ICM, Inc.	Royal Oak Charcoal
Biomass feedstock	hardwood	hardwood	hardwood	hardwood	hardwood
Pyrolysis technique	SP*	SP	gasification	gasification	SP
Pyrolysis temperature (°C)	600-650	600-650	500-575	550-650	600-650
Input biochar parameters					
Date of biochar application (mm/dd/yyyy)	10/15/2013	10/15/2013	10/15/2010	10/01/2009	05/14/2012
Amount of biochar applied (Mg ha^{-1})	0 - 90	0 - 90	0 - 112	0 – 9.3	0 - 22
Biochar incorporation depth (mm)	152	152	290	150	200
Sand	0.47	0.54	0.58	0.17	0.46
Clay	0.25	0.21	0.19	0.27	0.24
Calibrated parameters†					
Intercept DUL (α in Q_{DUL})	1.3067	1.3067	1.3067	4.134	3.2298
Intercept BD (α in Q_{BD})	1.3067	1.3067	1.4067	3.421	2.5456
Slope of DUL (K_{DUL})	1	0	0.33	0.12	0.1
Slope of BD (K_{BD})	1	0.05	0	0.04	0.05

*SP- slow pyrolysis

† Default parameters settings: Intercept DUL and BD = 1.3067, Slope of DUL (K_{DUL}) and BD (K_{BD}) = 0.33.

Biochar application rate impacted both the measured and predicted soil water and physical parameters (Fig. 8). The measured data showed greater variability in SWP than the predicted data in response to biochar application rate. This is because the measured data are influenced by complex interactions related to soil spatial variability that are not accounted for in the model. More specifically, model estimates of SAT, DUL, PAW, and OC systematically increase and BD estimates systematically decrease as biochar application rate increases, measured parameters follow the same general trends but show much more variability (Fig. 8). Further, the model predicted no change in LL due to biochar additions because the Q_{LL} in the biochar model has been set to one, as previously discussed. However, measured data indicate that biochar does affect LL with 4 of 5 sites showing an increasing trend in LL with increasing biochar application rate (Fig. 8). Specifically, at the highest biochar application rate at each site LL increased at the Boone, Bruner, Sorenson, and Lewis sites by 18 %, 6.5 %, 2.3 %, and 13.5

%, respectively, relative to the no biochar control. While LL decreased at all biochar application rates compared to the no biochar control at the Boyd site (Fig. 8).

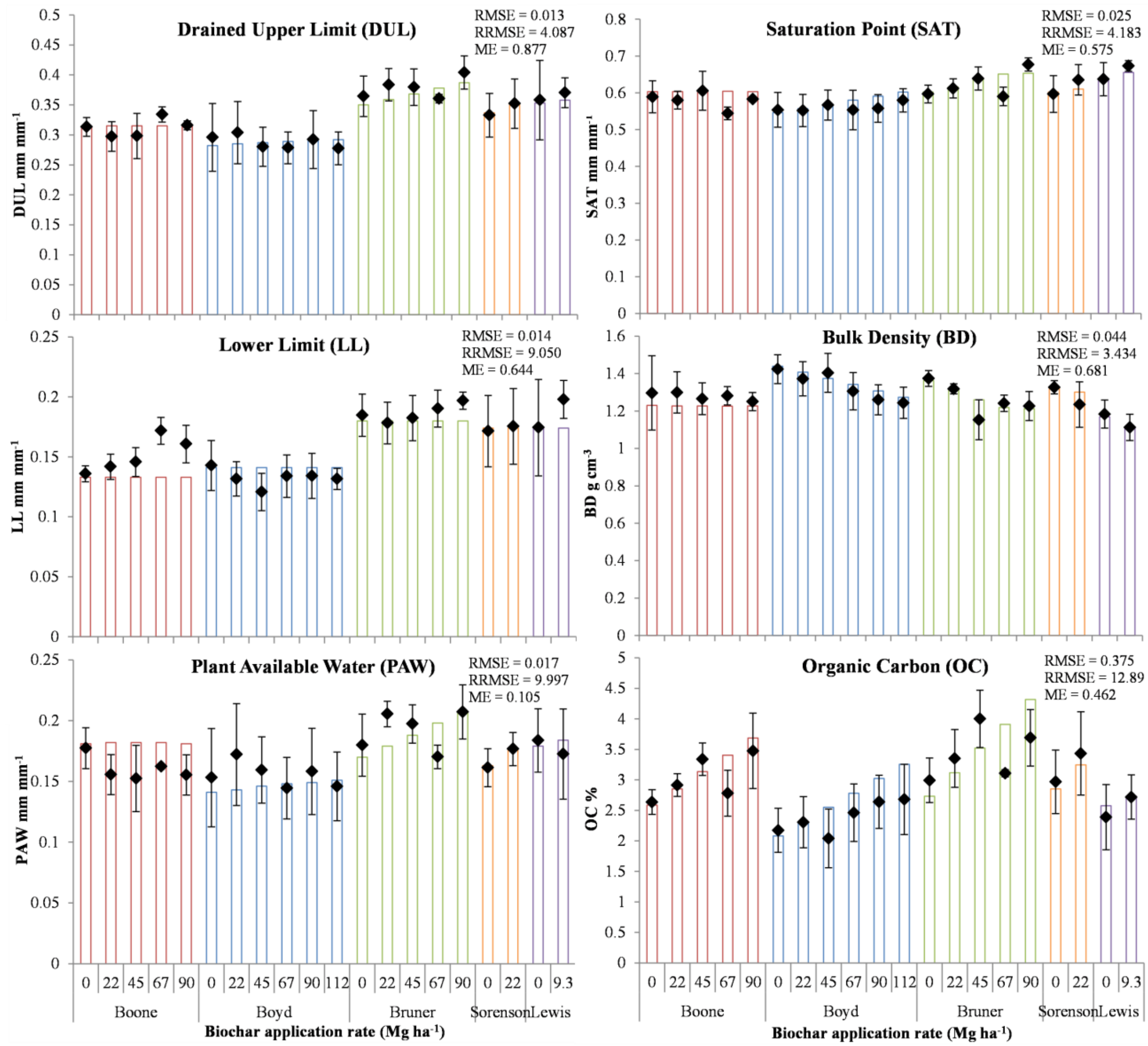


Fig. 8. APSIM biochar model predictions versus measurements of DUL, LL, PAW, SAT, BD, and OC. Bars represent the simulated data and points are the measured values with standard deviation bars.

For sites where variable impacts of biochar were observed (i.e. not biochar rate dependent) the intercept 1.3067 was not changed and only the slopes, K_{DUL} and K_{BD}, were adjusted to make subtle improvements in model performance. For example, at the Boone site (Fig. 1), the measured biochar impacts were opposite of the model predictions, we therefore set K_{DUL} and K_{BD} to one to minimize the predicted biochar impact (Table 3). Where uncalibrated model estimates were very low we increased the DUL and BD intercept values (i.e. Lewis and Sorenson sites) to increase initial soil water estimates for a given SOC content and then decreased the K value so the rate of change with increasing SOC was minimized. This adjustment led to improved model performance (Fig. 8).

Additionally, during calibration we found that tradeoffs exist in model estimates because the variables that influence soil water are linked. For example, when the default intercept value of 1.3067 for Q_{BD} was increased the relative magnitude of the resulting decrease in BD was much larger than the increase in SAT; however to optimize model performance we needed a larger increase in predicted SAT than BD. For the final calibration we tried to balance opposing impacts to obtain greatest model agreement.

Furthermore, the five biochar amended field sites had biochar of different ages (see 'date of biochar application' in Table 3). Thus, our results provide some indication of both short- and longer-term biochar impacts on SWP, which is important to consider in biochar studies. For example, six years after the application of biochar at the Boyd site, plots with the 22 Mg ha^{-1} and 112 Mg ha^{-1} biochar application rates had 6 % and 23 % higher levels of SOC, relative to the controls, respectively (Table 3; Fig. 8).

For all soil water parameters the calibrated model had the smallest RMSE and RRMSE and highest ME compared to the uncalibrated model (Table 4).

Table 4. Performance of the uncalibrated (default settings of Archontoulis et al., 2016) and calibrated modified biochar rate PTFs (see parameter values in Table 2)

	uncalibrated	***calibrated***	***uncalibrated***	***calibrated***	***uncalibrated***	***calibrated***
Parameter	*RMSE*		*RRMSE*		*ME*	
SAT	0.028	0.025	4.642	4.183	0.476	0.575
DUL	0.025	0.013	7.670	4.087	0.565	0.877
LL	0.014	0.014	9.050	9.050	0.644	0.644
BD	0.090	0.044	7.067	3.434	-0.351	0.681
PAW	0.512	0.017	302.1	9.997	-816.6	0.105

Discussion

This study brings a new soil database to the scientific literature that includes nearly 150 samples from soils with and without biochar. It includes soils that vary widely in textural class (Fig. 2) and for the first time provides insight into how biochar amended soils, to a depth of 30 cm, impact SWP as estimated by PTFs and how PTFs perform in top- and sub-soils. The soil samples were collected from five distinct soil associations and thus textural diversity was expected. Only one prior study has evaluated biochars impact on PTFs estimates on SWP using soils collected from the 0-5 cm depth interval (Lim et al., 2016). Additionally, the generated soils database can assist with subsequent studies comparing the performance of various PTFs for estimating SWP (e.g., the ensemble PTFs developed by Palmer et al. 2017).

In topsoils without biochar, the Saxton and Rawls (2006) PTFs were most robust in estimates of SAT and DUL, while the WSS database provided the best estimates of LL, BD, and PAW compared to the other PTFs examined. In topsoils with biochar, the soil parameters from the WSS database, when assessed by model robustness, provided the best estimates of biochar impacts on all soil water and physical parameters relative to the measured data (Table 1). The reason for WSS providing the majority of the best estimates for the SWP is not entirely known, but WSS generates SWP estimates based on numerous sampling points (and empirical corrections) within a soil series and not just an individual data point, which includes a greater amount of soil variability possibly contributing to more accurate estimates. The Saxton and Rawls (2006) PTFs underestimated SWP in topsoils with and without biochar compared to measured data (Fig. 4). The underestimation of PAW is especially important because this may adversely affect the ability of the APSIM model to predict crop yields. However, as these PTFs are averages across many measurements variability is expected, so the slope values near one and the similar positive trend for both soils with and without biochar is encouraging. Also, underestimation by the Saxton and Rawls (2006) equations for SWP such as SAT is of little importance because the APSIM model estimates SAT via its calculation of BD, which was predicted very well for both soils with biochar (slope = 1) and without biochar (slope = 0.98). Furthermore, all of the methods evaluated were developed using data from topsoils (e.g. Saxton and Rawls (2006) used soils only from the A-horizon) but we assessed their applicability for estimating SWP in subsoils to a depth of 90 cm. In general the PTFs were less accurate in estimating SWP in subsoils as more uncertainty was introduced (Figs. 6 and S4-S6).

During model calibration we found that the quality modifiers in the biochar model soil water equations are site specific as intercept and slope values must be calibrated for an individual field to obtain the best model fit (Table 2). Use of default values can result in overestimation or underestimation of biochars' actual impact on soil water and physical parameters at a given application rate and soil type. These results are consistent with interactions between biochar type and application rate, with soil, climate, crop, and management reported in the literature (Jeffery et al., 2011; Crane-Droesch et al., 2013; Laird et al., 2017). Local calibration is needed to optimally simulate the magnitude of biochar impacts on SOC and DUL. Alternatively, a better link between quality modifiers, biochar properties, and production methods is required to inform

APSIM biochar parameterization. However, the tradeoff between model estimates of BD and SAT was not fully consistent with trends in the measured data; hence a balance among quality modifiers was required to improve model performance. This finding suggests an area where the model itself could be improved. Also, determining that local calibration of the quality modifiers is necessary is an important finding because it will better inform subsequent model applications.

Both measured and predicted data showed a general increase in PAW with increasing SOM for topsoils with and without biochar. The measured data indicated an average 0.0012 mm increase in PAW per 0.1 % increase in SOC (Fig. 5), while the predicted data indicated an average 0.0013 mm increase in PAW per 0.1 % increase in SOC (data not shown). This finding is significant from a soil health perspective because it indicates that even a small increase in SOC improves PAW, which will assist in building more productive, resilient, and “climate-smart” soils (Paustian et al., 2016). Additionally, the results indicate that with the biochar quality modifiers, the APSIM biochar model soil water equations are better able to account for the rate of change in SWP with biochar application rate compared to the Saxton and Rawls (2006) PTFs. This may indicate that the impacts of biochar C on soil water in topsoils are not exactly the same as the impacts of biogenic SOC but further research is needed for confirmation. Similar results were obtained for the subsoils, with the measured data indicating a 0.0009 mm increase in PAW per 0.1 % increase in SOC and the predicted data showing a 0.0017 mm increase in PAW per 0.1 % increase in SOC (Fig. 6).

This study further provided some information about biochar stability and its impacts over time on soil water parameters. The biochar amended field sites evaluated here contained biochar that had been in soils for 1 to 6 years (Table 3). The same general trends were seen across all field sites for a given soil water or physical parameter regardless of biochar age. Future studies might consider examining soils amended with biochar for a longer period of time and see if the effects of biochar on SWP and the accuracy of the PTFs remains the same.

Future work should determine whether allowing the quality modifier for LL (Q_{LL}) and hence model predictions of LL to change in response to biochar additions will improve overall model performance. The APSIM biochar model is capable of estimating changes in LL over time similar to DUL and SAT but it currently is invariant for four reasons: 1) the change in LL is much smaller than the change in DUL, 2) LL is a more complex variable than DUL to estimate as it is related to the crop LL and water uptake by the roots, 3) evidence from previous studies showed no clear pattern of increase or decrease in LL as a function of biochar application rate, and 4) we aimed at modeling simplicity. However, the impact SOM has on estimates of LL is included in the Saxton and Rawls (2006) PTFs. Balland et al. (2008), also state that the LL should increase as both clay and SOM contents increase because SOM decreases BD and increases soil surface area, which should increase estimates of LL. Furthermore, other work on biochar amended soils specifically has shown that biochar can impact LL, but any effect is soil type dependent (Aller et al., 2017). Lastly, our measured data provides additional support for the hypothesis that biochar has an effect on LL, with 4 of 5 sites showing a consistent increase in LL with increasing biochar application rate (Fig. 8). This is likely attributed to the increase in surface area that results from biochar additions.

Conclusions

Pedotransfer functions are needed to estimate soil water parameters from soil properties and generate reliable model based predictions. Numerous PTFs have been developed to predict soil water dynamics based on SOM, but no prior studies have validated the use of PTFs for soils amended with biochar. We showed that the PTFs of Saxton and Rawls (2006) and the soil parameters from the WSS database were best for estimating the soil water and physical parameters evaluated in soils with and without biochar compared to the PTFs developed by Gijsman et al. (2003) and Palmer et al. (2017). Upon further examination of the Saxton and Rawls (2006) PTFs, results showed the same general increase in PAW with increasing SOM content for topsoils with and without biochar and a similar impact for subsoils. We also showed during calibration of the APSIM biochar model that the modified Saxton and Rawls (2006) PTFs that include quality modifiers to describe biochar impacts on soil water parameters improve model performance. However, we found that the quality modifiers are site-specific and local calibration is required to accurately predict the impacts of biochar on soil water parameters. Additionally, tradeoffs were found for some parameters (i.e. BD and SAT) when trying to optimize model performance, indicating that a balance must be established when adjusting the quality modifiers. Lastly, model simulations indicated that the LL increases with increasing biochar application rate, providing evidence that the Q_{LL} should not remain invariant in the biochar model; a point of future work. This study overall provided the necessary experimental verification of the PTFs originally developed by Saxton and Rawls (2006) for biochar amended soils. Our results advance efforts aimed at predicting biochars impacts on soil water relations and agroecosystem functioning as well as strengthen the APSIM biochar model for use in future studies.

Acknowledgments

This project is supported in part by the Global Climate and Energy Project, Stanford Subaward Agreement No. 60413992-112883-A, the National Science Foundation under Grant

Number EPS-1101284, the USDA-NIFA Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30411, and the USDA-NIFA Hatch project No. IOW03814.

References

Adams, W.A. 1973. The effect of organic matter on the bulk and true densities of some uncultivated podzolic soils. J. Soil Sci. 24:10-17. doi: 10.1111/j.1365-2389.1973.tb00737.x

Akhtar, S.S., G.T. Li, M.N. Andersen, and F.L. Liu. 2014. Biochar enhances yield and quality of tomato under reduced irrigation. Agric. Water Manag. 138:37-44. doi.org/10.1016/j.agwat.2014.02.016

Aller, D., S. Rathke, D. Laird, R. Cruse, and J. Hatfield. 2017. Impacts of fresh and aged biochars on plant available water and water use efficiency. Geoderma 307:114-121. doi.org/10.1016/j.geoderma.2017.08.007

Andales, A.A., W.D. Batchelor, C.E. Anderson, D.E. Farnham, and D.K. Whigham. 2000. Incorporating tillage effects into a soybean model. Agri. Syst. 66:69-98. doi.org/10.1016/S0308-521X(00)00037-8

Archontoulis, S.V., F.E. Miguez, and K.J. Moore. 2014a. Evaluating APSIM maize, soil water, soil nitrogen, manure, and soil temperature modules in the Midwestern United States. Agron. J. 106:1025-1040. doi:10.2134/agronj2013.0421

Archontoulis, S.V., F.E. Miguez, and K.J. Moore. 2014b. A methodology and an optimization tool to calibrate phenology of short-day species included in the APSIM PLANT model: application to soybean. Environ. Model. Software 62:465-477. doi.org/10.1016/j.envsoft.2014.04.009

Archontoulis, S.V., and F.E. Miguez. 2015. Nonlinear regression models and applications in agricultural research. Agron. J. 107(2):786-798.

Archontoulis, S.V., I. Huber, F.E. Miguez, P.J. Thorburn, and D.A. Laird. 2016. A model for mechanistic and system assessments of biochar effects on soils and crops and trade-offs. GCB Bioenergy. doi: 10.1111/gcbb.12314

Archontoulis, S.V., and M. Licht. 2016. A web platform for Forecasting and Assessment of Cropping sysTems (FACTS). Integrated Crop Management Newsletter, Iowa State University, http://crops.extension.iastate.edu/facts/

Atkinson, C.J., J.D. Fitzgerald, and N.A. Hipps. 2010. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. Plant Soil 337:1-18.

Balland, V., J.A.P. Pollacco, and P.A. Arp. 2008. Modeling soil hydraulic properties for a wide range of soil conditions. Ecol. Model. 219(3-4):300-316. doi.org/10.1016/j.ecolmodel.2008.07.009

Basche, A.D., S.V. Archontoulis, T.C. Kaspar, D.B. Jaynes, T.B. Parkin, and F.E. Miguez. 2016. Simulating long-term impacts of cover crops and climate change on crop production and environmental outcomes in the Midwestern United States. Agric. Ecosyst. Environ. 218:95-106. doi.org/10.1016/j.agee.2015.11.011

Basso, A., F.E. Miguez, D.A. Laird, R. Horton, and M. Westgate. 2013. Assessing potential of biochar for increasing water-holding capacity of sandy soils. GCB Bioenergy. 5:132-143. doi: 10.1111/gcbb.12026

Briggs, L. J., and H.L. Shantz. 1912. The wilting coefficient for different plants and its indirect determination. USDA. Bureau of Soils Bull.No. 230.USGPO, Washington,DC.

Brockhoff, S.R., N.E. Christians, R.J. Killorn, R. Horton, and D.D. Davis. 2010. Physical and mineral-nutrition properties of sand-based turfgrass root zones amended with biochar. Agron. J. 102:1627-1631. doi:10.2134/agronj2010.0188

Cheng, C-H., and J. Lehmann. 2009. Ageing of black carbon along a temperature gradient. Chemosphere 75(8):1021-1027. doi.org/10.1016/j.chemosphere.2009.01.045

Cornelissen, G., V. Martinsen, V. Shitumbanuma, V. Alling, G.D. Breedveld, D.W. Rutherford, M. Sparrevik, S.E. Hale, A. Obia, and J. Mulder. 2013. Biochar effect on maize yield and soil characteristics in five conservation farming sites in Zambia. Agron. J. 3(2):256-274. doi:10.3390/agronomy3020256

Crane-Droesch, A., S. Abiven, S. Jeffery, and M.S. Torn. 2013. Heterogeneous global crop yield response to biochar; a meta-regression analysis. Environ. Res. Lett. 8:1-8.

Dalgliesh, N., and M. Foale. 1998. Soil Matters: monitoring soil water and nutrients in dryland farming. Agricultural Production Systems Research Unit, Toowoomba, Old, Australia.

Dietzel, R., M. Liebman, R. Ewing, M. Helmers, R. Horton, M. Jarchow, and S.V. Archontoulis. 2016. How efficiently do corn- and soybean-based cropping systems use water? A systems modeling analysis. Glob. Change Biol. 22:666-681, doi: 10.1111/gcb.13101

Gai, C., H. Wang, J. Liu, L. Zhai, S. Liu, T. Ren, and H. Liu. 2014. Effects of feedstock and pyrolysis temperature on biochar adsorption of ammonium and nitrate. PLoS One, 9:e113888. doi:10.1371/journal.pone.0113888.

Gaskin, J.W., A. Speir, L.M. Morris, L. Ogden, K. Harris, D. Lee, and K.C. Das. 2007. Potential for pyrolysis char to affect soil moisture and nutrient status of a loamy sand soil. In Georgia Water Resources Conference, University of Georgia

Gee, G.W., and J.W. Bauder. 1986. Particle-size Analysis in Klute, A, (ed.), Methods of Soil Analysis Part 1, Physical and Mineral Methods Second Edition. ASA and SSSAJ, Madison, WI.

Gijsman, A., S. Jagtap, and J. Jones. 2003. Wading through a swamp of complete confusion: how to choose a method for estimating soil water retention parameters for crop models. Eur J Agron. 18:77-106. doi.org/10.1016/S1161-0301(02)00098-9

Gupta, S.C., and W.E. Larson. 1979. Estimating soil water retention characteristics from particle size distribution, organic matter percent, and bulk density. Water Resources Research. 15(6):1633-1635. doi:10.1029/WR015i006p01633

Hardie, M., B. Clothier, S. Bound, G. Oliver, and D. Close. 2014. Does biochar influence soil physical properties and soil water availability? Plant Soil 376 (1-2):347-361.

Herath, H.M.S.K., M. Camps-Arbestain, and M. Hedley. 2013. Effect of biochar on soil physical properties in two contrasting soils: an Alfisol and an Andisol. Geoderma 209-210:188-197. doi.org/10.1016/j.geoderma.2013.06.016

Holzworth, D.P., N.I. Huth, P.G. deVoil, E.J. Zurcher, N.I. Herrmann, G. McLean, K. Chenu, E.J. van Oosterom, V.O. Snow, C. Murphy, A.D. Moore, H. Brown, J.P.M. Whish, S. Verrall, J. Fainges, L.W. Bell, A.S. Peake, P.L. Poulton, Z. Hochman, P.J. Thorburn, D.S. Gaydon, N. Dalgliesh, D. Rodriguez, H. Cox, S. Chapman, A. Doherty, E. Teixeira, J. Sharp, R. Cichota, I. Vogeler, F.Y. Li, E. Wang, G.L. Hammer, M.J. Robertson, J.P. Dimes, A.M. Whitbread, J. Hunt, H. van Rees, T. McClelland, P.S. Carberry, J.N.G. Hargreaves, N.D. MacLeod, C.K. McDonald, J. Harsdorf, S. Wedgwood, and B.A. Keating. 2014. APSIM-evolution towards a new generation of agricultural systems simulation. Environ. Modell. Softw. 62:327-350. doi.org/10.1016/j.envsoft.2014.07.009

Hudson, B. 1994. Soil organic matter and available water capacity. J Soil Water Conserv. 49(2):189-194.

Iowa Environmental Mesonet. 2017. *Iowa Ag Climate Network*. Ames, IA: Iowa State University. Available at: http://mesonet.agron.iastate.edu/agclimate/ (accessed 24 March 2017).

Ippolito, J.A., D.A. Laird, and W.J. Busscher. 2012. Environmental Benefits of Biochar. J. Environ. Qual. 41. doi:10.2134/jeq2012.0151

Jeffery, S., F.G.A. Verheijen, M. van der Velde, and A.C. Bastos. 2011. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. Agric. Ecosyst. Environ. 144:175-187. doi.org/10.1016/j.agee.2011.08.015

Jones, J.W., J.M. Antle, B.O. Basso, K.J. Boote, R.T. Conant, I. Foster, H.C.J. Godfray, M. Herrero, R.E. Howitt, S. Janssen, B.A. Keating, R. Munoz-Carpena, C.H. Porter, C. Rosenzweig, and T.R. Wheeler. 2017b. Towards a new generation of agricultural system models, data, and knowledge products: state of agricultural systems science. Agric. Syst., 155:269-288. doi.org/10.1016/j.agsy.2016.09.021

Keating, B.A., P.S. Carberry, G.L. Hammer, M.E. Probert, M.J. Robertson, D. Holzworth, N.I. Huth, J.N.G. Hargreaves, H. Meinke, Z. Hochman, G. McLean, K. Verburg, V. Snow, J.P. Dimes, M. Silburn, E. Wang, S. Brown, K.L. Bristow, S. Asseng, S. Chapman, R.L. McCown, D.M. Freebairn, and C.J. Smith. 2003. An overview of APSIM, a model designed for farming systems simulation. Eur. J. Agron. 18: 267- 288. doi.org/10.1016/S1161-0301(02)00108-9

Klute, A. (ed.). 1986. Methods of soil analysis. Part I. 2nd ed. ASA. Monogr. No. 9, ASA and SSSA, Madison, WI.

Laird, D.A. 2008. The charcoal vision: A win–win–win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. Agron. J. 100:178-181. doi:10.2134/agrojnl2007.0161

Laird, D.A., P. Fleming, D.D. Davis, R. Horton, B. Wang, and D.L. Karlen. 2010. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. Geoderma 158:443-449. doi.org/10.1016/j.geoderma.2010.05.013

Laird, D.A., J.M. Novak, H.P. Collins, J.A. Ippolito, D.L. Karlen, R.D. Lentz, K.R. Sistani, K. Spokas, and R.S. Van Pelt. 2017. Multi-year and multi-location soil quality and crop biomass yield responses to hardwood fast pyrolysis biochar. Geoderma 289:46-53. doi.org/10.1016/j.geoderma.2016.11.025

Lehmann, J., J. Gaunt, and M. Rondon. 2006. Bio-char sequestration in terrestrial ecosystems- a review. Mitigation and Adaptation Strategies for Global Change. 11:403-427.

Lehmann, J., C. Czimczik, D. Laird, and S. Sohi. 2009. Stability of biochar in the soil. In J. Lehmann, S. Joseph (Eds.), Biochar for Environmental Management: Science and Technology, Earthscan, London (2009), pp. 183-205.

Lim, T.J., K.A. Spokas, G. Feyereisen, and J.M. Novak. 2016. Predicting the impact of biochar additions on soil hydraulic properties. Chemosphere 142:136-144. doi.org/10.1016/j.chemosphere.2015.06.069

Liu, J., H. Scjulz, S. Brandl, H. Miehtke, and B. Glaser. 2012. Short-term effect of biochar and compost on soil fertility and water status of a Dystric Cambisol in NE Germany under field conditions. J. Plant Nutr. Soil Sci. 175:698-707. doi:10.1002/jpln.201100172

Ma, L., L.R. Ahuja, S.A. Saseendran, R.W. Malon, T.R. Green, B.T. Nolan, P.N.S. Bartling, G.N. Flerchinger, K.J. Boote, and G. Hoogenboom. 2011. A protocol for parameterization and calibration of RZWQM2 in field research. In: Methods of Introducing System Models into Agricultural Research (eds Ahuja LR, Ma L), pp. 1-64. SSSA book series, Madison, WI.

Martinez-Feria, R.A., R. Dietzel, M. Liebman, M.J. Helmers, and S.V. Archontoulis. 2016. Rye cover crop effects on maize: a system-level analysis. Field Crops Res. 196:145-159. doi.org/10.1016/j.fcr.2016.06.016

Mia, S., F.A. Dijkstra, and B. Singh. 2017. Long-term aging of biochar: A molecular understanding with agricultural and environmental implications. Adv Agron. 141:1-51. doi.org/10.1016/bs.agron.2016.10.001

Nelson, D.W., and L.E. Sommers. 1982. Total carbon, organic carbon and organic matter. In: Page, A.L., R.H. Miller and D.R. Keeny. (eds.). Methods of Soil Analysis: Part 2 Chemical and Microbiological Properties. SSSA, Madison, WI, pp 539-579.

Nelson, D.W., and L.E. Sommers. 1996. Loss-on-ignition method. In: Bigham, J.M. (ed.). Methods of soil analysis, Part 3. Chemical methods. SSSA Book Series: 5, Madison, WI, pp 1004-1006

Nemes, A., Y. Pachepsky, and D. Timlin. 2011. Toward Improving Global Estimates of Field Soil Water Capacity. Soil Sci. Soc. Am. J. 75:807–812. doi:10.2136/sssaj2010.0251

Olness, A., and D. Archer. 2005. Effect of organic carbon on available water in soil. Soil Science. 170(2):90-101. doi:0038-075X/05/17002-90–101

Palmer, J., P.J. Thorburn, J.S. Biggs, E.J. Dominati, M.E. Probert, E.A. Meier, N.I. Huth, M. Dodd, V. Snow, J.R. Larsen, and W.J. Parton. 2017. Nitrogen cycling from increased soil organic carbon contributes both positively and negatively to ecosystem services in wheat agro-ecosystems. Front. Plant Sci. 8:731. doi: 10.3389/fpls.2017.00731

Paustian, K., J. Lehmann, S. Ogle, D. Reay, G.P. Robertson, and P. Smith. 2016. Climate-smart soils. Nature. 532:49-57. doi:10.1038/nature17174

Probert, M.E., J.P. Dimes, B.A. Keating, R.C. Dalal, and W.M. Strong. 1998. APSIM's water and nitrogen modules and simulation of the dynamics of water and nitrogen in fallow systems. Agric. Syst. 56:1-28. doi: 10.1016/S0308-521X(97)00028-0

Puntel, L.A., J.E. Sawyer, D.W. Barker, R. Dietzel, H. Poffenbarger, M.J. Castellano, K.J. Moore, P. Thorburn, and S.V. Archontoulis. 2016. Modeling long-term corn yield response to nitrogen rate and crop rotation. Frontiers in Plant Science, 7:1630. doi.org/10.3389/fpls.2016.01630

Rawls, W.J., D.L. Brakensiek, and K.E. Saxton. 1982. Estimation of soil water properties. Transactions of the ASAE. 25(5):1316-1320.

Rawls, W.J., Y.A. Pachepsky, J.C. Ritchie, T.M. Sobecki, and H. Bloodworth. 2003. Effect of soil organic carbon on soil water retention. Geoderma 116:61-76. doi.org/10.1016/S0016-7061(03)00094-6

Ritchie, J.T., J.R. Kiniry, C.A. Jones, and P.T. Dyke. 1986. Model inputs. In: Jones, C.A., Kiniry, J.R. (Eds.), CERESMaize: A Simulation Model of Maize Growth and Development, pp. 37-48.

Saxton, K.E., and W.J. Rawls. 2006. Soil water characteristic estimates by texture and organic matter for hydrologic solutions. Soil Sci. Soc. Am. J. 70:1569-1578. doi:10.2136/sssaj2005.0117

Schauberger, B., S.V. Archontoulis, A. Arneth, J. Balkovic, P. Ciais, D. Deryng, J. Elliott, C. Folberth, N. Khabarov, C. Mu¨ller, T.A.M Pugh, S. Rolinski, S. Schaphoff, E. Schmid, X. Wang, W. Schlenker, and K. Frieler. 2017. Consistent negative response of US crops to high temperatures in observations and crop models. Nature Communications 8:13931. doi: 10.1038/ncomms13931

Soil Survey Staff. 2004. National soil characterization data. NRCS National Soil Survey Center, Lincoln, NE.

Tammeorg, P., A.C. Bastos, S. Jeffery. et al., 2016. Biochars in soils: towards the required level of scientific understanding. J Environ Eng Landsc. doi.org/10.3846/16486897.2016.1239582

Thorburn, P.J., M.E. Probert, and F.A. Robertson. 2001. Modelling decomposition of sugarcane surface residues with APSIM-Residue. Field Crops Res. 70:223-232. doi:10.1016/S0378-4290(01)00141-1

Thorburn, P.J., E.A. Meier, and M.E. Probert. 2005. Modelling nitrogen dynamics in sugarcane systems: recent advances and applications. Field Crops Res. 92:337-352. doi:10.1016/j.fcr.2005.01.016

Twarakavi, N.K.C., M. Sakai, and J. Šimůnek. 2009. An objective analysis of the dynamic nature of field capacity. Water Resour. Res. 45:W10410. doi:10.1029/2009WR007944

Verheijen, F., S. Jeffery, A.C. Bastos, M. van der Velde, and I. Diafas. 2010. Biochar application to soils: a critical scientific review on effects on soil properties processes and functions. Joint Research Center (JRC), Scientific and Technical Report. Office for the Official Publications of the European Communities, Luxemberg.

Woolf, D., J.E. Amonette, F.A. Street-Perrott, J. Lehmann, and S. Joseph. 2010. Sustainable biochar to mitigate global climate change. Nature Communications. 1:1. doi:10.1038/ncomms1053.

Wösten, J.H.M., Y.A. Pachepsky, and W.J. Rawls. 2001. Pedotransfer functions: bridging the gap between available basic soil data and missing soil hydraulic characteristics. J Hydrol. 251:123-150. doi.org/10.1016/S0022-1694(01)00464-4

Zwieten, L.V., B.P. Singh, and J. Cox. 2012. Chapter four: Biochar effects on soil properties. In: J Cox (ed) Biochar in Horticulture: Prospects for the Use of Biochar in Australian Horticulture. Horticulture Australia, NSW Department of Primary Industries.

Appendix - supplementary data

Table S1. Details of the PTFs evaluated for estimating soil water and physical parameters in top-soils with and without biochar and subsoils.

Method and Equations Used	Comments
Saxton and Rawls (2006)	
$SAT= \theta_{33} + \theta_{(s-33)} – 0.097S + 0.043$	Equation 5 in Table 1 of Saxton and Rawls (2006), where θ_{33} is the moisture content determined at 33 kPa and S is %sand
$DUL= \theta_{33t} + (1.283(\theta_{33t})^2 -0.374(\theta_{33t})-0.015)$	Equation 2 in Table 1 of Saxton and Rawls (2006), where θ_{33t} is the moisture content, first solution, determined at 33 kPa. This DUL equation assumes normal density.
$LL = \theta_{1500t} + (0.14* \theta_{1500t} – 0.02)$	Equation 1 in Table 1 of Saxton and Rawls (2006), where θ_{1500t} is the moisture content, first solution, determined at 1500 kPa.
$BD = (1- \theta_s)*2.65$	Equation 6 in Table 1 of Saxton and Rawls (2006), where θ_s is SAT.
PAW= DUL-LL	
Palmer et al. (2017)	
SAT= 0.95 (1-BD/2.65)	Units of $m^3 m^{-3}$. Calculated from Dalgliesh and Foale (1998) and assumes soil particle density = 2.65.
$DUL= a + b*SOC + c*SOC^2$	a,b, and c are constants that estimate gravimetric water content for a given matric potential and are based on textural class. See supplementary materials of Palmer et al. (2017). SOC = SOM/1.72 (Nelson and Sommers, 1982)
$LL= a + b*SOC + c*SOC^2$	a,b, and c are constants that estimate gravimetric water content for a given matric potential and are based on textural class. See supplementary materials of Palmer et al. (2017). SOC = SOM/1.72 (Nelson and Sommers, 1982)
$BD = 100/((\%SOM/BD_{SOM}) + (100-\%SOM/BD_m))$	Calculate the mineral fraction using $BD_m = (1 – SOMf)/((1/BD) – (SOMf/BD_{SOM}))$ given that the BD_{SOM}= 0.224 (g cm^{-3}). Calculation based on Adams (1973). BD has units of g cm^{-3}.
PAW= DUL-LL	

Table S1. Continued

Gijsman et al. (2003)	
SAT =0.95*porosity	Equation adapted from Rawls et al., 1982
DUL =0.2576-(0.002*sand)+(0.0036*clay)+(0.0299*%OM)	Equation adapted from Rawls et al., 1982
LL_1= 5 + 0.0244*%clay^2 LL_2= 3.62 + 0.444*%clay	LL_1 is used for soils that have a %sand content > 70%. LL_2 is used for all other soils. Equations adapted from Ritchie et al. 1986
BD = 2.65-(SAT/0.95)	
PAW_1=0.423-0.00381*sand PAW_2=0.1079+0.0005004*silt	PAW_1 is for soils with >75% sand. PAW_2 is for soils with >70% silt and all other soils.
Web Soil Survey	
SAT= (1-BD/2.65)	
DUL	Soil properties and qualities →soil physical properties→ water content at -1/3 bar
LL	Soil properties and qualities →soil physical properties→ water content at -15 bar
BD	Soil properties and qualities →soil physical properties→ determined at -1/3 bar. Units of g cm^{-3}
PAW	Soil properties and qualities →soil physical properties→ available water supply, 0-50 cm

Table S2. Biochar parameters adjusted during model set-up and calibration for the 5 sites where biochar was applied.

Description	Value (Boone)	Value (Bruner)	Value (Boyd)	Value (Lewis)	Value (Sorenson)
Date of biochar application (mm/dd/yyyy)	10/15/2013	10/15/2013	10/15/2010	10/01/2011	05/14/2012
amount of biochar applied (Mg ha^{-1})	0 - 90	0 - 90	0 - 112	0 – 9.3	0 - 22
fraction carbon in biochar	0.76	0.76	0.78	0.63	0.76
fraction of biochar lost during application	0.3	0.02	0.4	0.02	0.2
mean residence time for labile biochar pool	1	1	1	1	1
mean residence time for resistant biochar pool	500	500	500	500	500
biochar labile fraction	0.13	0.13	0.13	0.13	0.13
fraction of decomposed biochar that goes to OC pools	0.4	0.4	0.4	0.4	0.4
fraction of decomposed biochar that goes to biom	0.05	0.05	0.05	0.05	0.05
biochar C:N ratio	232	232	132	151	232
sand	0.47	0.54	0.58	0.17	0.46
clay	0.25	0.21	0.19	0.27	0.24
priming coefficient for biom pool	0	0	0	0	0
priming coefficient for hum pool	0	0	0	0	0
priming coefficient for cell pool	0	0	0	0	0
priming coefficient for carb pool	0	0	0	0	0
priming coefficient for lign pool	0	0	0	0	0
negative priming coefficient for internal C partitioning, biom	0	0	0	0	0
negative priming coefficient for internal C partitioning, biom	0	0	0	0	0
negative priming for internal C partitioning, fom	0	0	0	0	0
negative priming for internal C partitioning, fom	0	0	0	0	0
C:N ratio of biom pool	8	8	8	8	8
C:N ratio of soil stuff	12	12	12	12	12
Biochar incorporation depth (mm)	152	152	290	150	200
Intercept dul	1.3067	1.3067	1.3067	4.134	3.2298
Intercept bd	1.3067	1.3067	1.4067	3.421	2.5456
Slope of dul quality equation (default 0.33)	1	0	0.33	0.12	0.1
Slope of bd quality equation (default 0.33)	1	0.05	0	0.04	0.05
Biochar LV	50	50	50	50	50
Biochar ECEC	187	187	187	187	187
Biochar cnrf coefficient	0.693	0.693	0.693	0.693	0.693
Optimum C:N ratio for biochar	25	25	25	25	25
Biochar WFPS factor	1	1	1	1	1
Biochar NH_4 absorption coefficient	0.006	0.006	0.006	0.006	0.006
Biochar NH_4 desorption coefficient	0.006	0.006	0.006	0.006	0.006

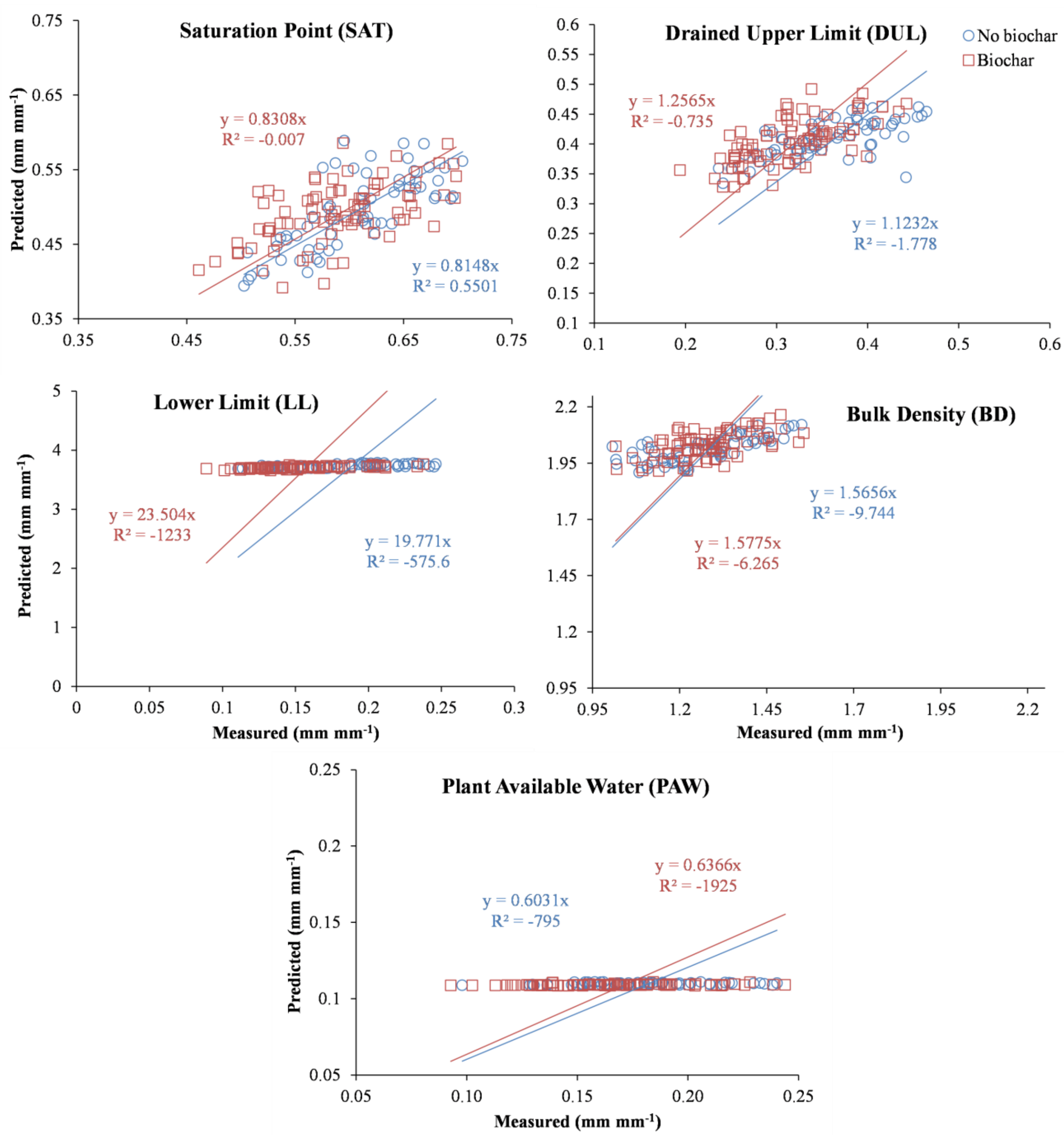


Fig. S1. Measured versus predicted soil water and physical parameter values estimated using the Gijsman et al., (2003) PTFs for soils from the 0-5, 5-15, and 15-30 cm depth increments, with biochar (N=85) and without biochar (N=61).

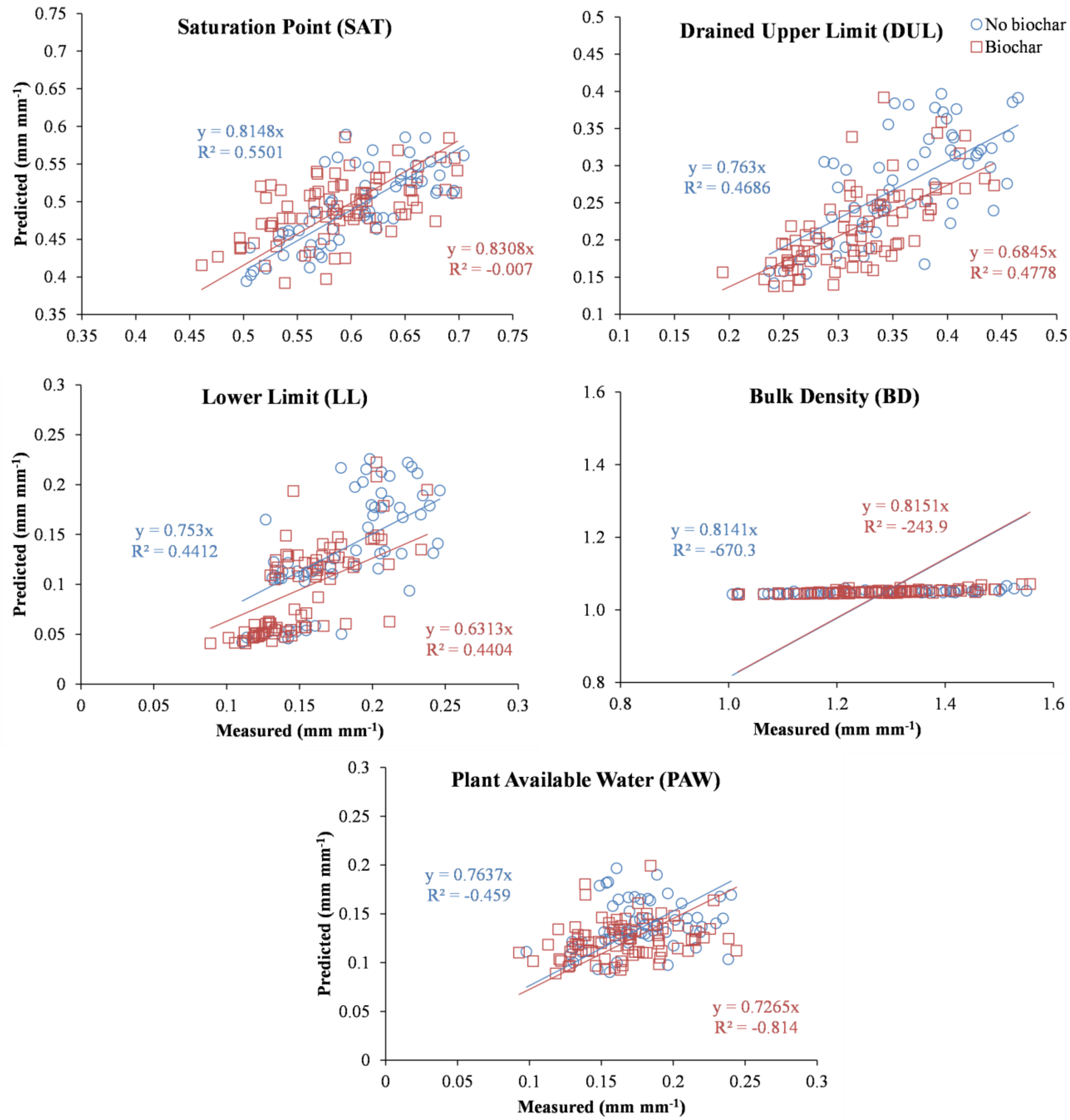


Fig. S2. Measured versus predicted soil water and physical parameter values estimated using the ensemble PTFs of Palmer et al., (2017) for soils from the 0-5, 5-15, and 15-30 cm depth increments, with biochar (N=85) and without biochar (N=61).

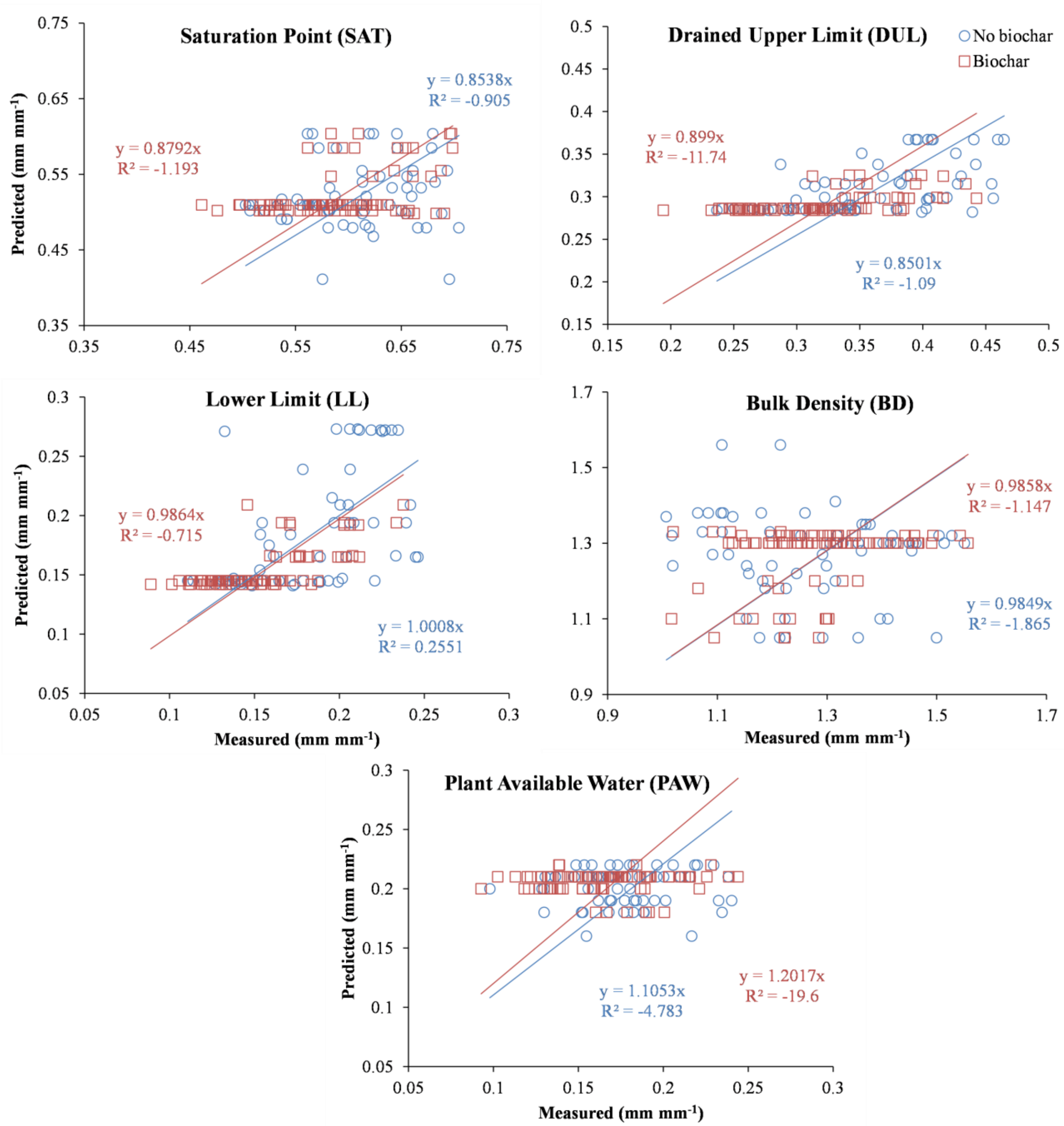


Fig. S3. Measured versus predicted soil water and physical parameter values estimated using the WSS database for soils from the 0-5, 5-15, and 15-30 cm depth increments, with biochar (N=85) and without biochar (N=61).

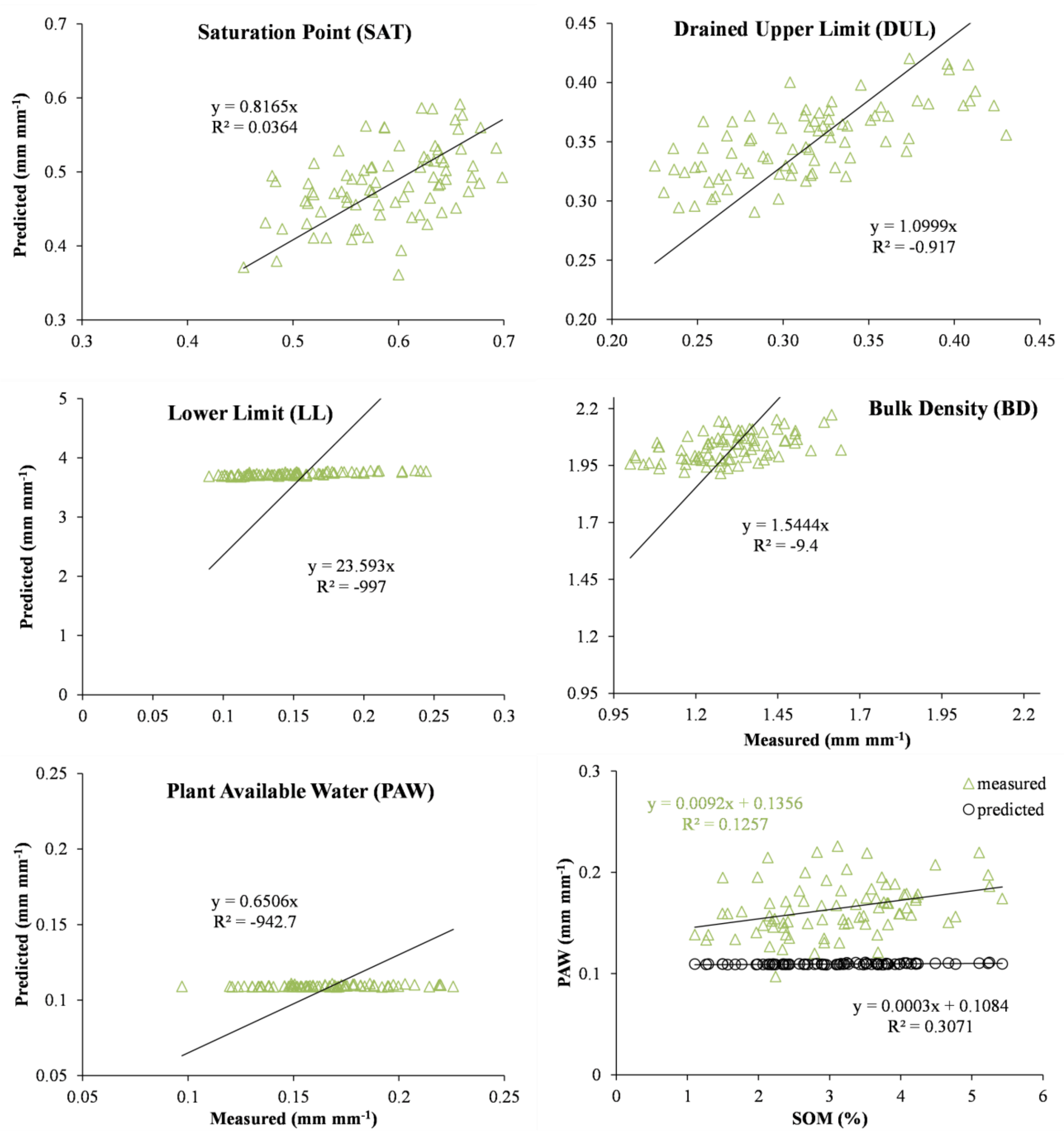


Fig. S4. Measured versus predicted soil water and physical parameter values and estimates of the relationship between SOM and PAW using the Gijsman et al., (2003) PTFs for subsoils (N=80).

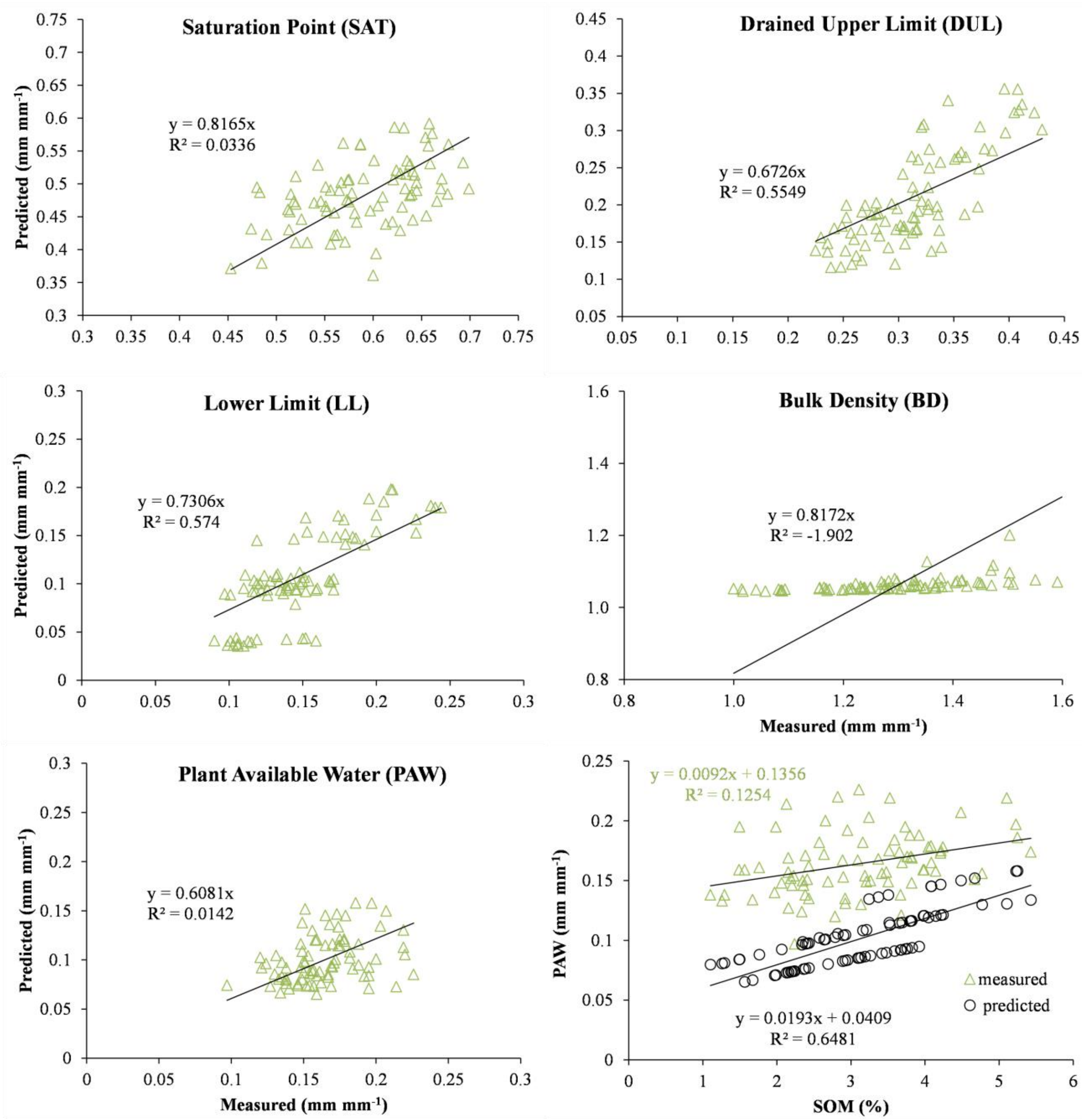


Fig. S5. Measured versus predicted soil water and physical parameter values and estimates of the relationship between SOM and PAW using the ensemble PTFs of Palmer et al., (2017) for subsoils (N=80).

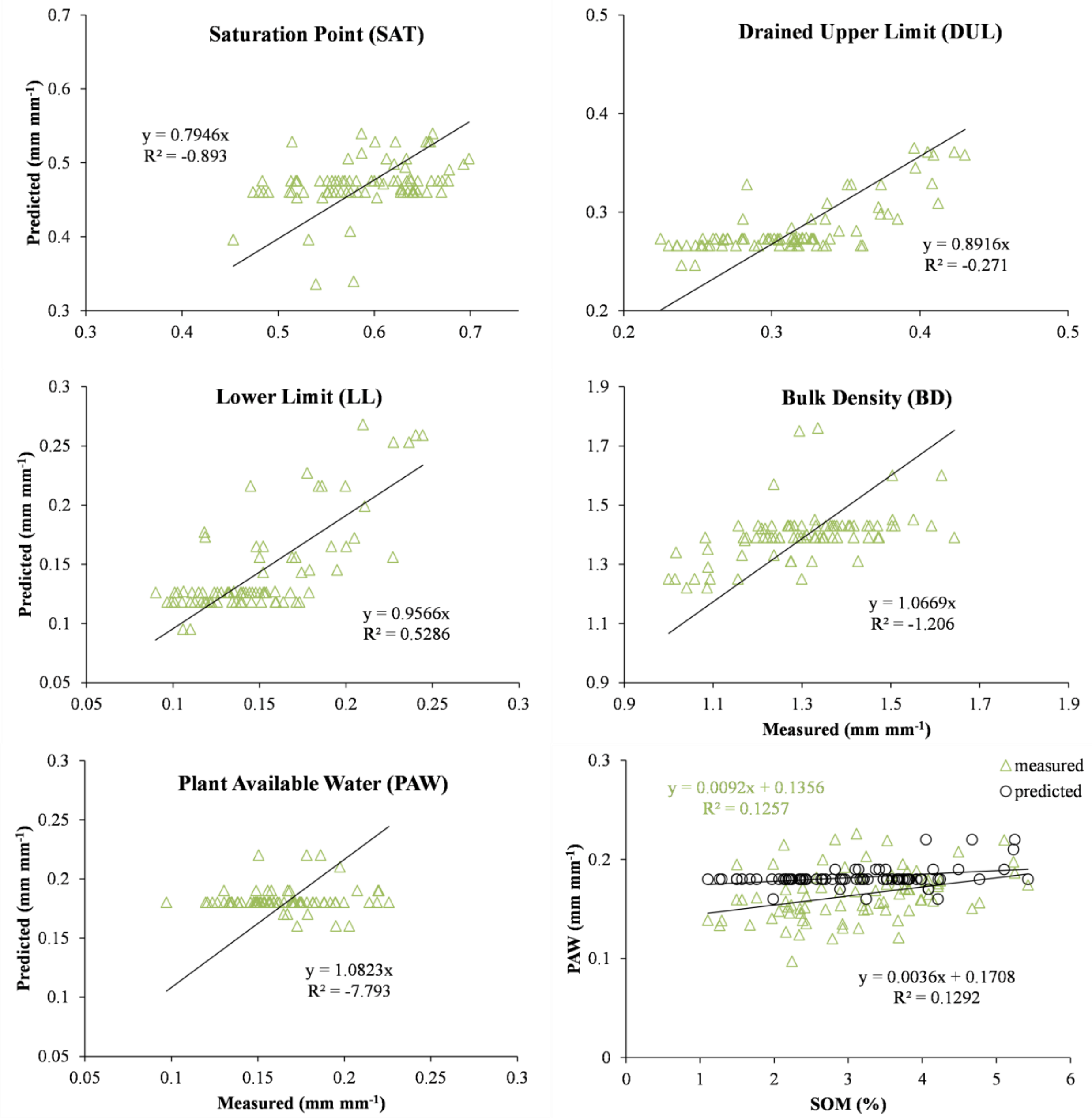


Fig. S6. Measured versus predicted soil water and physical parameter values and estimates of the relationship between SOM and PAW using the WSS database for subsoils (N=80).

CHAPTER 6. OPTIMIZING BIOCHAR APPLICATION RATES FOR MIDWEST CORN-BIOENERGY CROPPING SYSTEMS

Modified from a manuscript to be submitted to Field Crops Research

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Abstract

The Agricultural Production Systems sIMulator (APSIM) is a farming systems model capable of integrating many aspects of agro-ecosystem complexity to predict the long-term effects of crop production systems and management practices on crop yields and environmental quality. A biochar model was recently developed within the APSIM platform to simulate the effects of biochar and enhance understanding of biochars' long-term impacts on agro-ecosystem performance. Midwestern farms are the largest potential source of crop residues for bioenergy production, however, there is a need for new more sustainable practices to compensate for the negative effects of residue harvesting on soil quality. Biochar applications could offset the potential negative effects of residue removal and enhance agricultural productivity while simultaneously sequestering carbon. We used soil, crop yield, and management data from a long-term field study in central Iowa that includes residue removal and crop rotations, to calibrate and validate the APSIM biochar model. We then applied the model to identify the optimum biochar application rate that maximizes productivity and environmental performance of conventional corn and corn-soybean cropping systems in Iowa under different N fertilizer application rates

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and residue harvesting scenarios. A cost-benefit analysis was also employed to identify the economically optimal biochar application rate from both producer and societal perspectives. Results of model applications showed that across all scenarios as biochar application rate increased both continuous corn and corn-soybean rotations reduced nitrate leaching, increased soil carbon levels, and a small impact on corn yields. The cost-benefit analysis revealed that public benefits, evaluated from decreased nitrate leaching and increased soil carbon levels, significantly outweighed the private revenue accrued from crop yield gains, and a lower biochar application rate (22 Mg ha^{-1}) was more cost-effective (per ton) compared to higher biochar rates. Overall, biochar applications can eliminate negative effects of residue harvesting on soil quality and are an economically viable option for a farmer when at least 50% of the residue is harvested for sale; which can be done sustainably.

Keywords: biochar, APSIM, corn yields, residue harvesting, economic analysis, sustainability

Abbreviations: APSIM, Agricultural Production Systems sIMulator; CC, continuous corn; CS, corn-soybean; C, carbon; GDD, growing degree days; ME, modeling efficiency; NO_3, nitrate; RMSE, root mean square error; RRMSE, relative root mean square error; SOC, soil organic carbon

Introduction

Agriculture lies at the nexus of the food, water, and energy sectors. Nexus challenges are driven by increasing population pressure and emergent economies which are increasing demand for food and energy production while accelerating degradation of soil and water resources and changes in global climate (FAO, 2014). Agricultural producers are left with the challenge of increasing food production, providing biomass for bioenergy production, and using freshwater more efficiently; all while reducing their environmental footprint. To begin addressing the food-water-energy challenges in agriculture, new long-term sustainable agricultural practices need to be developed using a systems approach which considers the complex interactions of agriculture and the environment.

The US Midwest is one of the largest and most productive agricultural regions globally; producing nearly one-third of the world's corn (*Zea mays* L.) and soybean (*Glycine max* L.) crops (FAOSTAT, 2015). In Iowa specifically, corn for grain is planted on nearly 14 million acres and soybeans on more than 9 million acres (USDA-NASS, 2016), covering roughly 80% of the landscape (Newton and Kuethe, 2015). As the number of acres devoted to growing corn and soybean has increased in response to rising feed, fuel, fiber, and food demands, cropping system diversity has largely been eliminated (Liebman et al., 2013). This has potentially negative consequences as more diverse systems that include long-term rotations are well known to have widespread benefits for soil and environmental quality; impacts which have been widely reported on (Giller et al., 1997; Karlen et al., 2006; Russell et al., 2006; Davis et al., 2012; Liebman et al., 2013; Lal, 2015; Aller et al., 2017).

Additionally, the shift to finding alternative energy sources has meant not only corn grain but corn residue is a high value product. A US Department of Energy report in 2005 estimated biomass recovered from crop residues could significantly contribute to US energy production (Perlack et al., 2005). With residues from Midwestern farms representing the highest concentration of biomass for bioenergy production. Previously, crop residues were returned to the soil for conservation purposes. Residues left in the field have many positive impacts on soil and ecosystem functioning including: maintaining soil organic matter, reducing soil erosion by wind and water, and increasing soil microbial activity and carbon levels (Wilhelm et al., 2007; Lal and Pimentel., 2007; Blanco-Canqui and Lal, 2009; Laird and Chang, 2013). Soil quality and long-term agricultural productivity will be negatively impacted if crop residues are continuously removed in an unsustainable way (Wilhelm et al., 2004; Laird and Chang, 2013). Some of the potential negative effects of residue removal, however, could be offset through the incorporation of soil amendments. Biochar, the charcoal like co-product of biomass pyrolysis, is a soil amendment which can enhance soil quality and agricultural productivity while simultaneously sequestering carbon (Laird et al., 2009; Lehmann and Joseph, 2015).

Farming systems models such as the Agricultural Production Systems sIMulator (APSIM) are capable of integrating the complexity of the agro-ecosystem to predict the long-term effects of changing crop production strategies and management practices on crop yields and environmental quality. APSIM uses an advanced modeling platform that integrates numerous agricultural inputs and parameters to simulate crop, soil, management, and environment interactions, helping to facilitate a systems level of understanding (Keating et al., 2003; Holzworth et al., 2014). APSIM uses various component models (e.g., soil, crop, water, management) linked to a central engine to simulate the growth and productivity of over 40 crop species and soil processes. For Iowa agriculture, the corn and soybean crop, residue, soil water, soil C and N models have all been calibrated and validated to simulate growth, productivity, and environmental impacts (Malone et al., 2007; Archontoulis et al., 2014a,b; Basche et al., 2016; Dietzel et al., 2016; Martinez-Feria et al., 2016).

Recently a biochar model was developed within the APSIM platform (Archontoulis et al., 2016) to simulate the effects of biochar amendments and to enhance understanding of biochars' long-term impacts on agro-ecosystem performance. The model is publically available through the APSIM platform (version 7.9, released April 2017). Initial biochar model testing was conducted using experimental data from only one study (Rogovska et al., 2014), with preliminary results suggesting very good agreement between simulations and experimental observations (Archontoulis et al., 2016). However, additional testing of the new biochar model across different locations, management systems, and weather years is required to increase confidence before the model is widely used for decision-making and agricultural assessments.

The goal of our research is to test further and ultimately validate the APSIM biochar model. The specific objectives of this study were to; 1) use soil, crop yield, and management data from a long-term field study that includes continuous corn and corn-soybean rotations and biomass harvesting for bioenergy production in central Iowa to calibrate the APSIM biochar model, and 2) use the calibrated biochar model to identify the optimum biochar application rate that maximizes grain and biomass productivity and environmental performance of corn and corn-soybean cropping systems in Iowa under different management scenarios. We hypothesized that biochar applications can offset the negative effects of residue harvesting, as evaluated by SOC levels and NO_3 leaching rates, while not impacting corn yields.

Materials and Methods

Dataset and Measurements

The experimental dataset used was collected from a crop rotation experiment conducted at Iowa State University's Sorenson Research Farm in Boone County, IA from 2006-2016. The study investigated the effects of several cropping systems, corn in rotation with triticale (*Triticosecale* cv. Pronghorn) or switchgrass (*Panicum virgatum* cv. Cave-in-Rock), continuous corn, and corn-soybean rotations, and biochar applications on crop yields and soil quality. The data from this study was selected for use because we have a continuous record (11 years) of end-of-season grain and stover yields along with soil quality data and site management information. A detailed description of the study site and an assessment of impacts of crop rotations and biochar amendments on soil quality have been presented previously (Aller et al., 2017).

In brief, the field study was arranged in a completely randomized block design with split plots that included five different crop rotations: continuous corn, corn-soybean, corn-soybean-triticale/soybean-corn-soybean-triticale/soybean, corn-corn-corn/switchgrass-switchgrass-switchgrass-switchgrass, and continuous switchgrass. Rotations were in a six-year cycle with all phases of each rotation present every year in four replicate blocks and with complete removal of aboveground biomass from all plots containing corn, switchgrass, and triticale every year. There were a total of 208 plots, 112 whole plots, and 192 subplots. Of the 112 whole plots, 16 were in continuous switchgrass and were never split into subplots (no biochar applications), while the other 96 whole plots were split. Biochar was applied on one-half of each split plot over four consecutive years (2012, 2013, 2014, and 2015) following the corn-phase of the rotations; thus representing a temporal series of field-aged biochar. A slow-pyrolysis hardwood biochar (#10 granular charcoal, Royal Oak Enterprises, LLC., Roswell, GA) was applied at a rate of 22.4 t ha^{-1} and was incorporated with a single pass of a rotary tiller to a depth of 20 cm.

Only two of the five experimental rotations are considered here: continuous corn (CC) and corn-soybean (CS) rotation. We chose these two rotations because together they comprise 93% of the cropping systems in Iowa (USDA-NASS, 2016) and the corn and soybean models in APSIM are well developed, while the new switchgrass model for APSIM (Ojeda et al., 2017) requires further testing and calibration. Additionally, biochar applications in 2012, 2013, and 2014 were evaluated for the CC system and in 2012 and 2013 only for the CS rotation system because of the timing at which biochar applications were made in the respective cropping system.

Daily weather information came from the Iowa Environmental Mesonet (2017), which reports data from a weather station approximately 2 km north of the field site. The baseline soil profile used in the model was the Clarion soil series (Fine-loamy, mixed, superactive, mesic Typic Hapludolls) as this is the dominant soil series at the site. Soil parameters were updated based on analysis of samples collected from the field site (Aller et al., 2017). Parameters adjusted included the drained upper limit (DUL), lower limit (LL), saturation point (SAT), bulk density (BD), and soil organic carbon (SOC). We used the average of SOC measurements for all 0-30 cm samples collected from no-biochar plots between 2006-2016. SOC values for the remainder of the soil profile, 30-220 cm, as well as values for the entire soil profile for DUL, LL, and BD were based on analysis of deep cores collected in 2016. The soil profile parameter values can be found in the supplementary material (Tables S1 and S2).

The APSIM Model - Initialization and Calibration

APSIM version 7.9 was initialized by selecting the following models: Corn and Soybean crop models (Keating et al., 2003), Soil N (soil N and C cycling model with the default soil temperature model; Probert et al., 1998), SoilWat (a tipping bucket soil water model; Probert et al., 1998); SURFACEOM (residue model; Probert et al., 1998; Thorburn et al., 2001, 2005); the Biochar model (Archontoulis et al., 2016), and the following management activities: planting, harvesting, fertilization, tillage, and crop rotations (Keating et al., 2003).

Management practices specified for each crop within APSIM included rules for crop rotations, tillage, biochar tillage (to incorporate the biochar immediately after application in the plots and years applicable), sowing, fertilizing, and harvesting. Nitrogen fertilizer was applied at a rate of 190 kg ha^{-1} annually for continuous corn and 135 kg ha^{-1} in corn years only for the corn-soybean rotation. A 110-day relative maturity corn hybrid and a maturity group 2 soybean variety were used for the APSIM simulations (Archontoulis et al., 2014a, 2014b).

The biochar model was included in simulations for plots where biochar was applied. Within the biochar model we added the following management information: timing of application, amount of biochar applied, depth of biochar incorporation; and measured soil and biochar parameter information: sand and clay content, biochar carbon fraction, biochar labile fraction, and biochar C:N ratio (Aller et al., 2017). All other biochar parameter values were derived from Archontoulis et al. (2016). All biochar parameter values are presented in the supplementary material (Table S3).

To initiate the SOC and soil N pools across the profile, we ran simulations for 6-years prior to the start of the analyzed simulations, similar to Dietzel et al. (2016). The initial 6-years of simulated data were excluded from model analysis and corn yield and SOC values were output. Soybean yields were not analyzed in this study.

During model initialization we used early season plant stand counts for the plant-sowing density parameter rather than seeding rates. This additional management information improved agreement between measured and predicted yields because the model assumes that the number of plants sown equals the number harvested. It does not account for plant losses between sowing and harvest due to management practices (e.g., poor germination) or environmental factors (e.g., frost).

We changed that following maize model cultivar specific parameters: 1) time from emergence to the end of vegetative stage was increased from 214 to 250 growing degree days (GDD), 2) time from flowering to maturity was decreased from 885 to 820 GDD, 3) time from flowering to the start of grain fill was increased from 150 to 170 GDD, and 4) time from maturity to ripening was increased from 1 to 180 GDD. The new cultivar parameter values are presented in the supplementary data (Table S4). The maize hybrid used in the field experiment was changed during the experimental period (2006 – 2016) but the relative maturity group (110-day) remained the same. A total of forty-eight plots were used in model calibration (N = 48) for each of the CC and CS rotation systems.

Model Application

The calibrated APSIM biochar model was used to determine the optimum application rate of biochar under various management conditions for CC and CS rotation systems. Specifically, we evaluated three different nitrogen application rates (75, 150, and 225 kg N ha^{-1}) and three residue removal rates (0, 50, and 90 % removal) against increasing application rates of biochar

(0, 22, 45, 90 Mg ha^{-1}) for both cropping systems. In addition, the scenarios were run for both a high carbon, high C:N ratio biochar (e.g. hardwood, slow pyrolysis) and a low carbon, low C:N ratio biochar (e.g. corn stover, fast-pyrolysis). In both cropping systems nitrogen fertilizer was only applied to the corn crop. Sequential simulations were run over a 37-year period (1980-2016), with the first five years (1980-1984) prior to biochar application excluded from the analysis. The model outputs included corn yield (kg ha^{-1}), SOC (%), and NO_3-N leaching below the root zone.

Data Analysis

Agreement between simulated and measured values was assessed using the root mean square error (RMSE), relative root mean square error (RRMSE), and modeling efficiency (ME) statistics.

$$RMSE = \sqrt{\frac{\sum_{i-1}^{N}(S-O)^2}{N}} \tag{1}$$

$$RRMSE = \frac{RMSE}{O_{avg}} * 100 \tag{2}$$

$$ME = 1 - \frac{\sum(S-O)^2}{\sum(O-O_{avg})^2} \tag{3}$$

where N is the total number of observations, S is the simulated value, O is the measured value, and O_{avg} is the average of the measured values. Lower values of RMSE and RRMSE indicate better model fit, as they provide the absolute and relative error between the simulated and measured values, respectively. However, RMSE and RRMSE have a lower limit because the simulated error can never be lower than the inherent error in the measured data used for model calibration (He et al., 2017). Modeling efficiency (scale <0-1), which describes the average model performance across all observations (Archontoulis and Miguez, 2015), was determined as an indicator of overall goodness of fit. Model efficiency is useful when comparing model performance between different datasets because it normalizes the data (Wallach, 2006).

Economic Analysis

A cost-benefit analysis using a partial budget approach was employed to evaluate the private and public net economic benefits of the various biochar application and corn stover removal rate scenarios over the 32-year simulation period (1985-2016). We used the agronomic and environmental outcomes of 36 scenarios and assigned literature-driven values to determine the economic costs and benefits relative to the respective baseline scenario for each cropping system (Calkins and Dipietre, 1983). The baseline scenarios represented the 2.75 ha experimental field site that had no biochar, no residue removal, and an N application rate of 225 kg N ha^{-1} every year in the CC system and 150 kg N ha^{-1} in corn years of the CS rotation system. We generated the net private and public benefits across all 32 years following the application of biochar in 1985. This entailed varying the C:N ratio of the biochar (high or low), the biochar application rate, application rate of N fertilizer, and rate of residue removal in both the CC and CS rotation systems. From the analysis we also determined the private and public breakeven costs, which represents the maximum per-ton price of biochar the producer could afford to pay.

Net private benefits

The net private benefits were determined from increased[1] cash crop yields relative to the baseline plus net-revenues due to the sale of corn stover. Annual historical CPI-adjusted corn and soybean prices and a constant stover price were used (Johanns, 2017; Edwards, 2014**)**. The $13 per ton net-revenue from corn stover removal was determined from the price of stover as feed minus the farmers harvest and transportation costs. We assumed that the private costs were labor and machinery expenses from a one-time biochar application, plus the additional cost of nitrogen beyond the rate applied in the respective baseline scenarios for each system. We also assumed that all other corn and soybean production costs were identical across the 2.75 ha field in all scenarios[2]. The net private benefits acquired annually and summed over the 32-year period were calculated using 2015 dollar values by the following equation:

Net private benefits = value from yield increase + value from sale of stover – biochar application cost

To calculate the private breakeven cost for a farmer applying biochar, the net private benefits were divided by the quantity of biochar applied in each scenario. The final value represents the maximum price a farmer would pay to not lose any revenue by applying biochar, relative to the baseline scenario.

[1] If cash crop yields decrease, most often because of lack of nitrogen, we consider the negative benefit to be an added cost
[2] That is, the fixed and variable costs are identical across scenarios, and would only potentially vary with respective to acreage.

Net public benefits

The net public benefits were determined from the reduction in NO_3-N leaching and the increase in SOC, which was given a value based on the corresponding reduction in CO_2 emissions from each cropping system. We quantified the value of decreased NO_3-N leached relative to the baseline scenario annually using an equilibrium price implied from water quality trading, $3.13 for each pound nitrate saved (Ribaudo et al., 2014), and summed that over the 32-year simulation period for each scenario. The reduction in CO_2 emitted for each scenario was taken as the difference in SOC in 2016 and in 1985, relative to the difference from the baseline scenario, assuming that for every ton increase in SOC there is one less ton of CO_2-C emitted in the future. The economic value of future CO_2 emission reductions was converted into a dollar amount using a $36 per ton social cost of carbon and a 3% discount rate (Nordhaus, 2017). Annual net public benefits were calculated using the following equation:

Net public benefits = value of reduced NO_3-N leaching + reduced CO_2 emissions through improvements in SOC

Total net benefits

The total net benefits were calculated as the sum of the net private benefit and net public benefit. The public breakeven cost for each scenario was calculated as the total net benefits divided by the quantity of biochar applied in each scenario. This value represents the maximum price at which it would benefit all of society, including the farmer, if the farmer applied biochar. Lastly, the potential benefits associated with changes in land value were not included in the analysis.

Results

Model Performance - Corn Yields

The calibrated model performed well for simulating corn yields in both the CC and CS rotation systems (Fig. 1). In the CC system, RMSE decreased from 3168 to 1482 kg ha^{-1}, the RRMSE from 34.6 to 16.2%, and the ME increased from -1.03 to 0.56 between the uncalibrated and calibrated models, respectively. Similarly in the CS rotation, the RMSE decreased from 2415 to 1526 kg ha^{-1}, the RRMSE from 23.5 to 14.7%, and the ME increased from -0.3 to 0.49 from the uncalibrated to calibrated model, respectively.

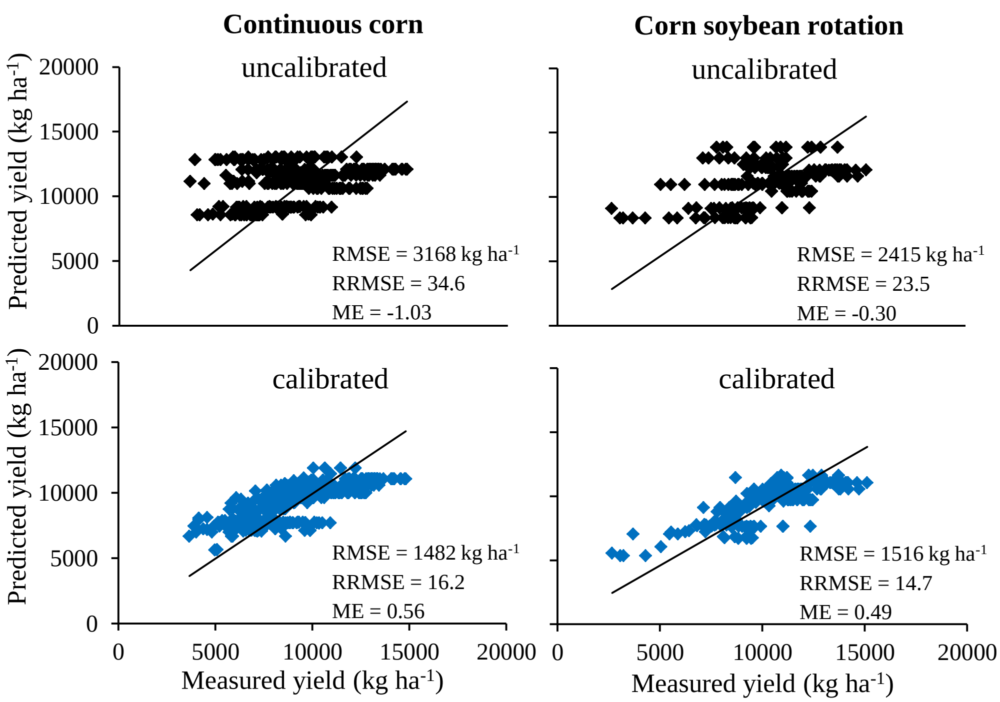

Fig. 1. Model calibration summary figures for the CC and CS rotation systems (N = 528 for each cropping system).

When the data were averaged over the no-biochar control plots, year-to-year variability in corn yields were simulated well by the model (Fig. 2). Only in 2006 and 2015 were the predicted compared to measured yields largely underestimated for both cropping systems. For the CC simulations the relative error was higher and ME was lower compared to the CS rotation (RRMSE = 15.9 and ME = 0.57 for CC versus RRMSE = 15.03 and ME = 0.60 for CS rotation). Therefore, the overall average model performance was better for the CS than the CC system.

Model performance in response to biochar applications was evaluated. Model results show satisfactory agreement between measured and predicted yields following different years of biochar application (Fig. 3). For the CC system, both measured and predicted grain yields increased following biochar application for the three different years biochar was applied (2012, 2013, and 2014) (Fig. 3). A similar increase was observed for the control plots (Fig. 3), however, the yield increase in the biochar plots, as determined from the measured data, was 837, 943, and 760 kg ha^{-1}, in 2012, 2013, and 2014, compared to the no-biochar controls, respectively (data not shown). But this observed yield increase in the biochar plots is confounded by tillage and thus may not be a true biochar effect. In the 2012 and 2013 biochar application years the model showed greater error and lower ME compared to their respective controls. Model performance was equal when the 2014 biochar and no-biochar control plots were evaluated with the RRMSE = 17 and the ME = 0.5.

For the CS rotation the model showed similar results as for the CC system (Fig. S1). Average corn yields were underpredicted in a couple years for each of the 2012 and 2013 plots. The relative model error and the ME were lower in the 2012 biochar plots (RRMSE = 13.6 and ME = 0.31) compared to the no-biochar controls (RRMS = 15.8 and ME =0.62). In the 2013 treatments, the biochar plots show greater relative model error relative to the control plots (RRMSE = 15.3 versus RRMSE = 15.2) and lower ME (ME = 0.14 versus ME = 0.52).

Indicating that overall model performance is better at estimating corn yields in the control plots then the biochar plots for the CS rotation system (Fig. S1).

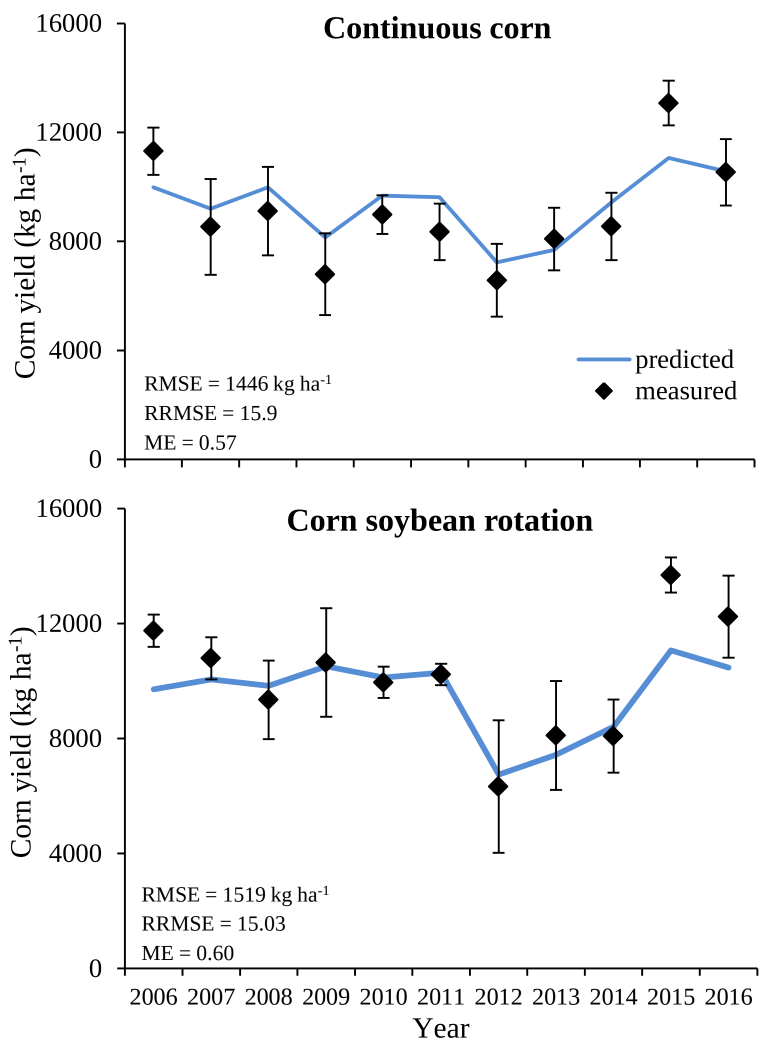

Fig. 2. Corn yield (kg ha^{-1}) over 11 years in the CC and CS rotation systems. Measured values (black diamonds) are the average of all control plots with standard deviation bars. Predicted yields are represented by the blue line.

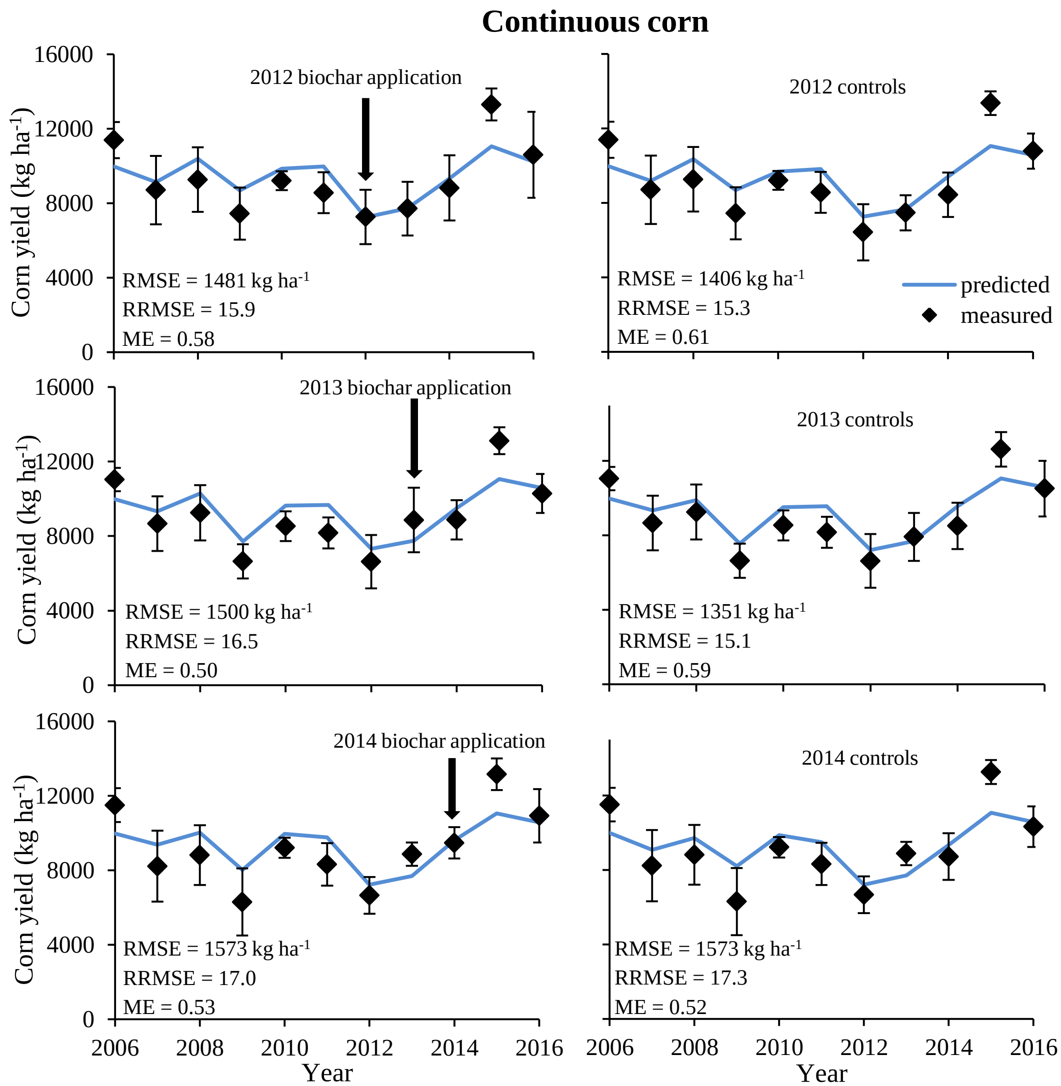

Fig. 3. Corn yields as impacted by three different field ages of biochar under CC (biochar applied in 2012, 2013, or 2014). Measured values (black diamonds) are the average of all plots with biochar (left side) and no-biochar control plots (right side) with standard deviation bars across all 11 years. Predicted yields are represented by the blue line.

Model Performance- Soil Organic Carbon

The model in general overpredicted average SOC levels in the control plots for both the CC and CS rotation systems across the 11 years analyzed (Fig. 4). For the CC system the relative model error was lower, RRMSE = 25.9, compared to the CS rotation system, RRMSE = 27. 4. The ME was much better in the CS rotation (ME = -0.1) than in the CC system (ME = -1.2) showing better overall model agreement in the CS rotation. However, the large RRMSE values, > 20%, and the negative ME values for both cropping systems indicates poor overall model performance and that the average of the observed data is better than the model predictions. Further, in both systems model predictions of SOC varied little, while measured data were more variable (Fig. 4). This is attributed to sampling variability from field measurements.

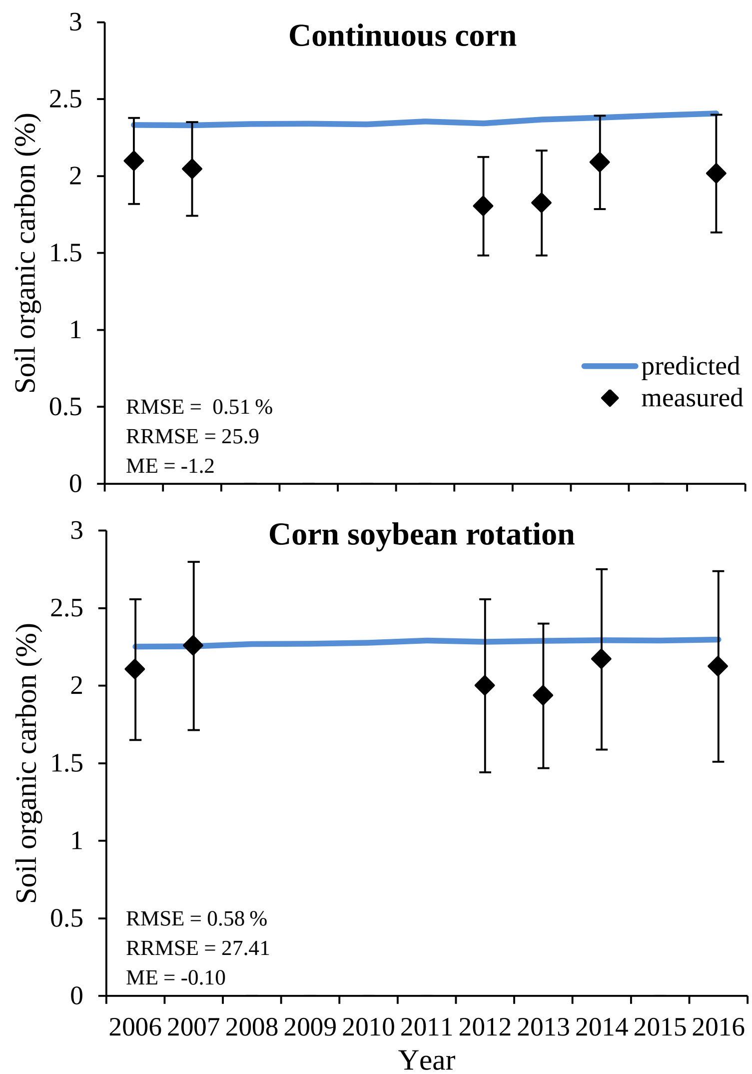

Fig. 4. Percent soil organic carbon over 11 years under CC and CS rotation systems. Measured values (black diamonds) are the average for all control plots with standard deviation bars. Predicted yields are represented by the blue line.

Model performance separated by biochar application year revealed that model goodness of fit was better in the plots with biochar than the no-biochar controls plots for both the CC (Fig. 5) and the CS rotation systems (Fig. S2). However, the model on average overpredicted

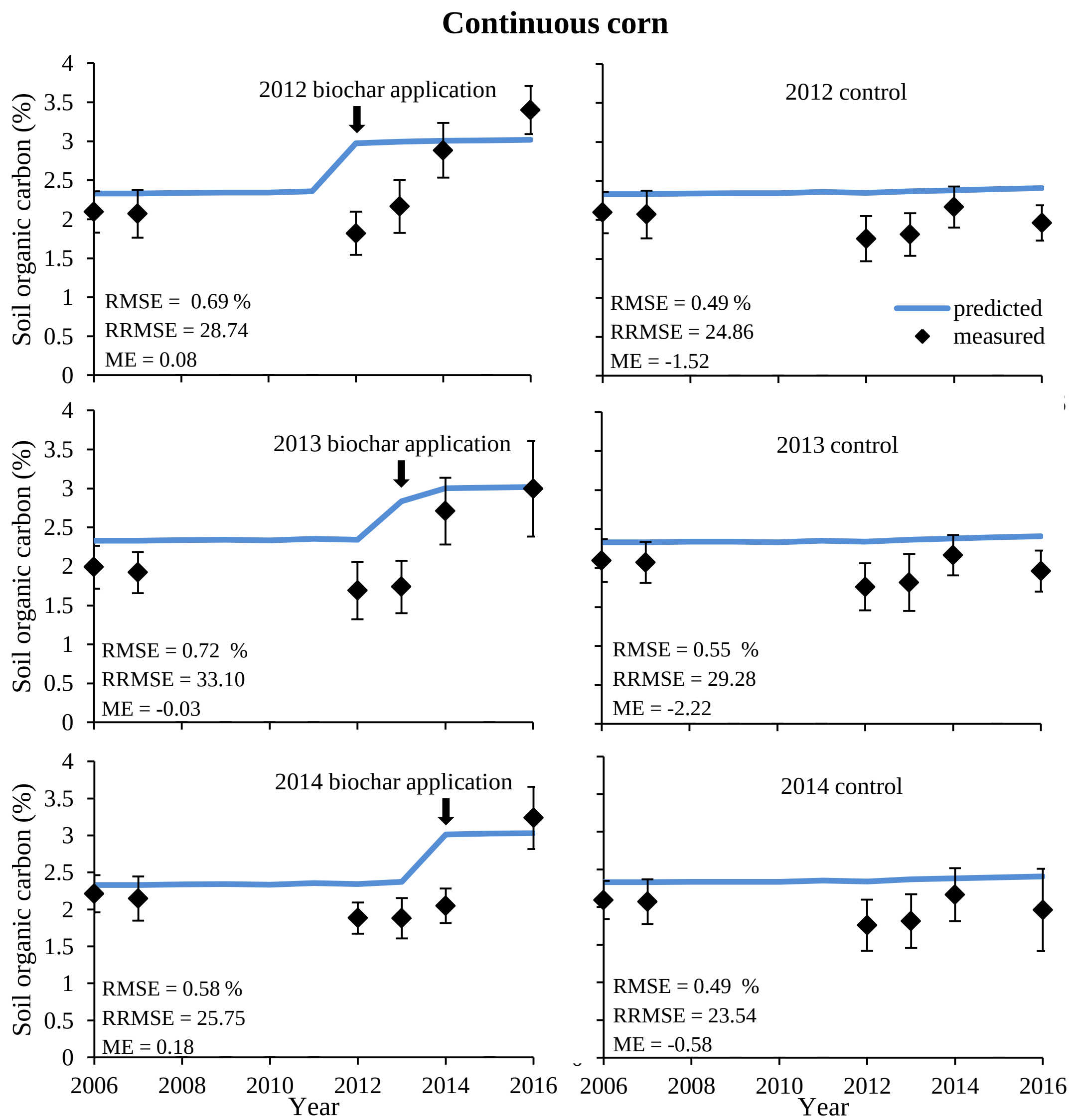

Fig. 5. Percent SOC across 11 years as impacted by three different field ages of biochar (biochar applied in 2012, 2013, or 2014) for the CC system. Measured values (black diamonds) are the average of all plots with biochar (left side) and no-biochar control plots (right side) with bars showing standard deviations. Predicted yields are represented by the blue line.

SOC levels in both biochar and no-biochar control plots for both cropping systems. For the CC system, model agreement between the predicted and measured SOC data was best for the 2014 biochar application year, with the RRMSE = 25.8 and the ME = 0.18. But for all three years and for both biochar and no-biochar control plots, RRMSE was > 20 % and ME was negative, except ME values for the 2012 and 2014 biochar plots which were positive. This again indicates poor overall performance of the model at estimating SOC. Similar results were observed for the CS rotation, as the model almost always overpredicted SOC compared to the measured data (Fig. S2). Although, ME was improved for both the biochar and no-biochar control plots in the CS system compared to the CC system.

Model Application - Agronomic Impacts

The impacts of the high and low C biochar treatments on corn yields (calculated as the average % difference between biochar and no-biochar control treatments over the 32-year simulation) were similar, with only a decreased magnitude of change relative to the control observed for the low C biochar compared to the high C biochar treatments (Fig. 6). Corn yields evaluated by cropping system showed different trends based on residue removal rates for the 75 and 150 kg N ha^{-1} fertilization rate scenarios (Fig. 6). For the CC system, at the 75 kg N ha^{-1} fertilization rate, a residue removal rate of 0% resulted in the largest yield decline followed by the 90% and then 50% residue removal rates, regardless of biochar application rate. At the same fertilization rate but for the CS rotation system, a residue removal rate of 50% resulted in the largest yield decline followed by the 90% and then 0% residue removal rates, regardless of biochar application rate. At the 150 kg N ha^{-1} fertilization rate corn yields were decreased at all biochar application and residue removal rates compared to the no-biochar control for the CC system. Whereas in the CS rotation system corn yields were positive for the 0% and 50% residue removal rates and negative for the 90% residue removal rate regardless of biochar application rate (Fig. 6). The APSIM model is very sensitive to soil N status, hence these differences are attributed to biochar and crop residue effects on N immobilization/mineralization. Specifically, the model predicts that N immobilization will decrease N availability to the crop while the labile C in biochar is being mineralized. The effect of biochar treatments on corn yields was positive at the 225 kg N ha^{-1} fertilization rate regardless of biochar application and residue removal rates (Fig. 6). At the 225 kg N ha^{-1} fertilization rate, N availability is no longer limiting to crop growth and hence the positive aspects of biochar on soil quality boost yields.

Overall the changes in average corn yields attributable to biochar were small over the 32-year simulation period and across all scenarios. The largest simulated effect was a yield decline of 2.66% for the CC system with application of 90 Mg ha^{-1} high C biochar, 0% residue removal, and a fertilization rate of 75 kg N ha^{-1} (Fig. 6), which would put the corn crop under considerable N stress. The 2.66% yield loss equates to a total of 6112 kg ha^{-1} (97 bu ac^{-1}) over the entire 32-year simulation period. When the low C biochar was applied the greatest yield decline was below -2% in the CC system scenario of 75 kg N ha^{-1}, 0% residue removal, and 90 Mg ha^{-1} biochar (Fig. 6). The difference is attributed to the lower C:N ratio of the low C biochar relative to the high C biochar, which means less N immobilization during mineralization of the labile C in the biochar.

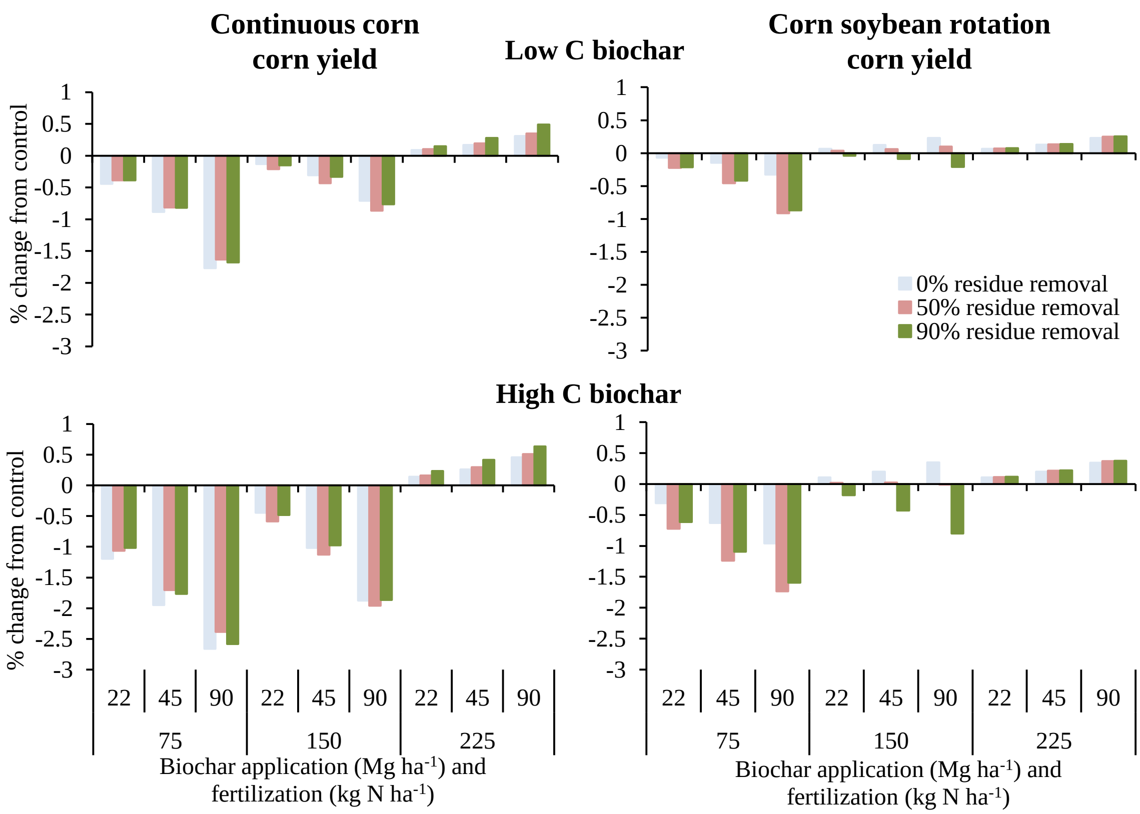

Fig. 6. Differences in average corn yields (kg ha^{-1}) between biochar and no-biochar control treatments for the 32 year simulation (1985-2016) in CC and CS rotation systems under different N fertilization and residue management scenarios and when low/high C content and C:N ratio biochars were applied in 1985.

For both cropping systems and biochar types the simulations showed the same patterns but different intensities for the impacts of various management scenarios on NO_3 leaching (Fig. 7). All NO_3 leaching values were calculated as the average % difference between the biochar and no-biochar control treatments over the 32-year simulation period. Simulation results indicate that application of both the high and low C biochars decreased NO_3 leaching through the root zone for all N fertilization and residue removal scenarios and for both cropping systems (Fig. 7). The percent reduction in NO_3 leaching relative to the no-biochar controls increased with the N fertilization rate and the amount of biochar applied. The maximum impact on NO_3 leaching for both cropping systems was a reduction of about 10% when the low C biochar was applied and a nearly 20% reduction when the high C biochar was applied (Fig. 7). This difference is attributed to the C:N ratio of the biochar and the availability of biochar C for N immobilization. Residue removal decreased NO_3 leaching for the 75 and 150 kg N ha^{-1} N fertilization rates, by contrast residue removal increased NO_3 leaching for the 225 kg N ha^{-1} fertilization rate. These differences are attributed to N being limiting to the crop at the 75 and 150 kg N ha^{-1} N fertilization rates, but as more residue is removed the availability of N increases, enhancing root growth and reducing NO_3 leaching. Whereas, at the 225 kg N ha^{-1} fertilization rate, N is not limiting plant or root growth, thus as residue removal increases less N is immobilized and NO_3 leaching increases.

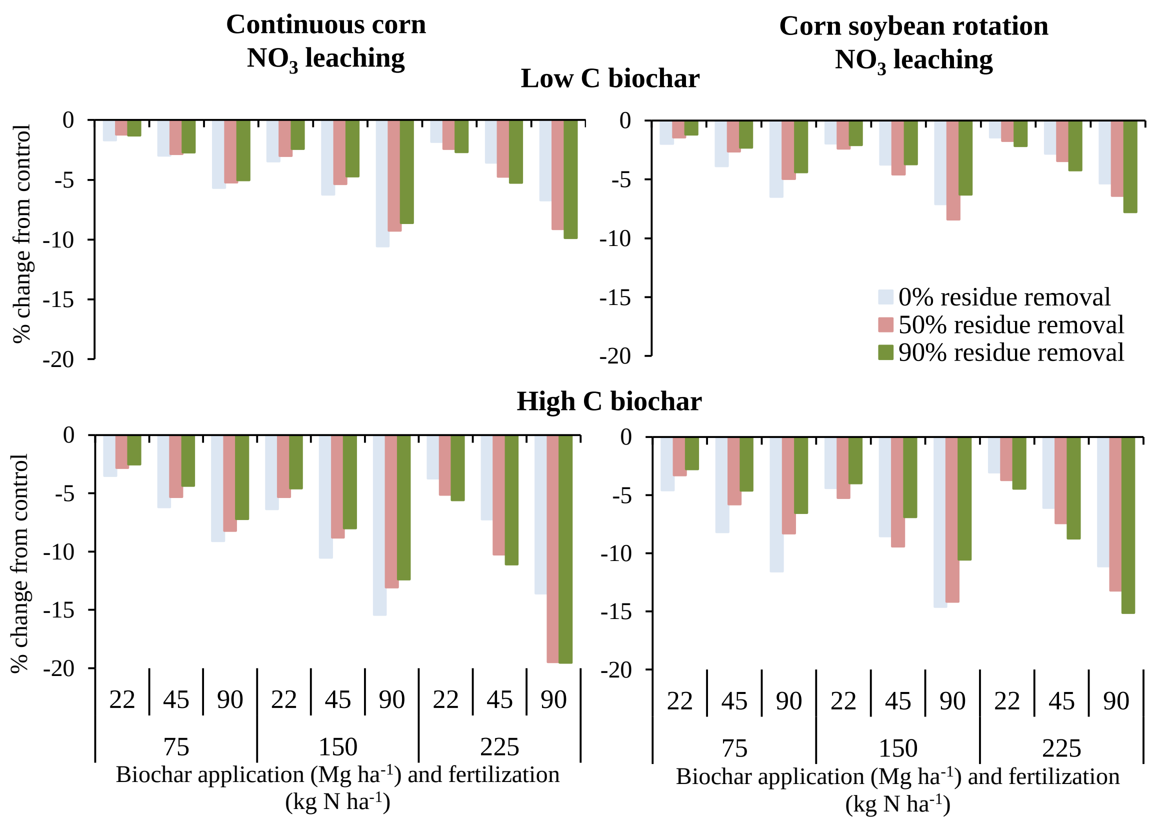

Fig. 7. Average difference in NO_3 leaching for the 32 year simulation (1985-2016) between biochar and no-biochar control treatments for the CC and CS rotation systems under different N fertilization and residue management scenarios and when low/high C content and C:N ratio biochars were applied in 1985.

For both the CC and CS rotation systems and biochar types, the simulations showed the same patterns but different intensities for the impacts of the various management scenarios on SOC levels (Fig. 8). Here, we determined the % difference in SOC levels relative to baseline SOC levels, between 1985 (pre-biochar application) and 2016 (32 years after biochar application). The model indicates that biochar applications had the same impact on SOC levels in both the CC and CS rotation systems for the various N-fertilization and crop residue removal scenarios (Fig. 8). There was a direct relationship between biochar application rate and the increase in SOC content at the end of the 32-year simulation. For the scenarios with 22, 45, 90 Mg ha^{-1} biochar application rates, as percent residue removal increased, the percent increase in SOC levels decreased but were higher than the initial SOC levels because of the biochar C. For the no-biochar control scenarios, SOC levels increased over time for the 0% residue removal treatment but decreased over time for the 50% and 90% residue removal treatments. When the low C biochar was applied, the simulations indicate a smaller increase in SOC levels over 32 years relative to the simulations using the high C biochar. This observation is attributed to the lower C content and C:N ratio of the low C biochar. In addition, for these simulations the coefficient that models biochars effect on biogenic SOC turnover rates (priming effect), was set to zero. Changing the priming coefficient to induce a positive or negative effect from biochar, increased or decreased mineralization of biogenic SOC, respectively, will likely alter the results observed.

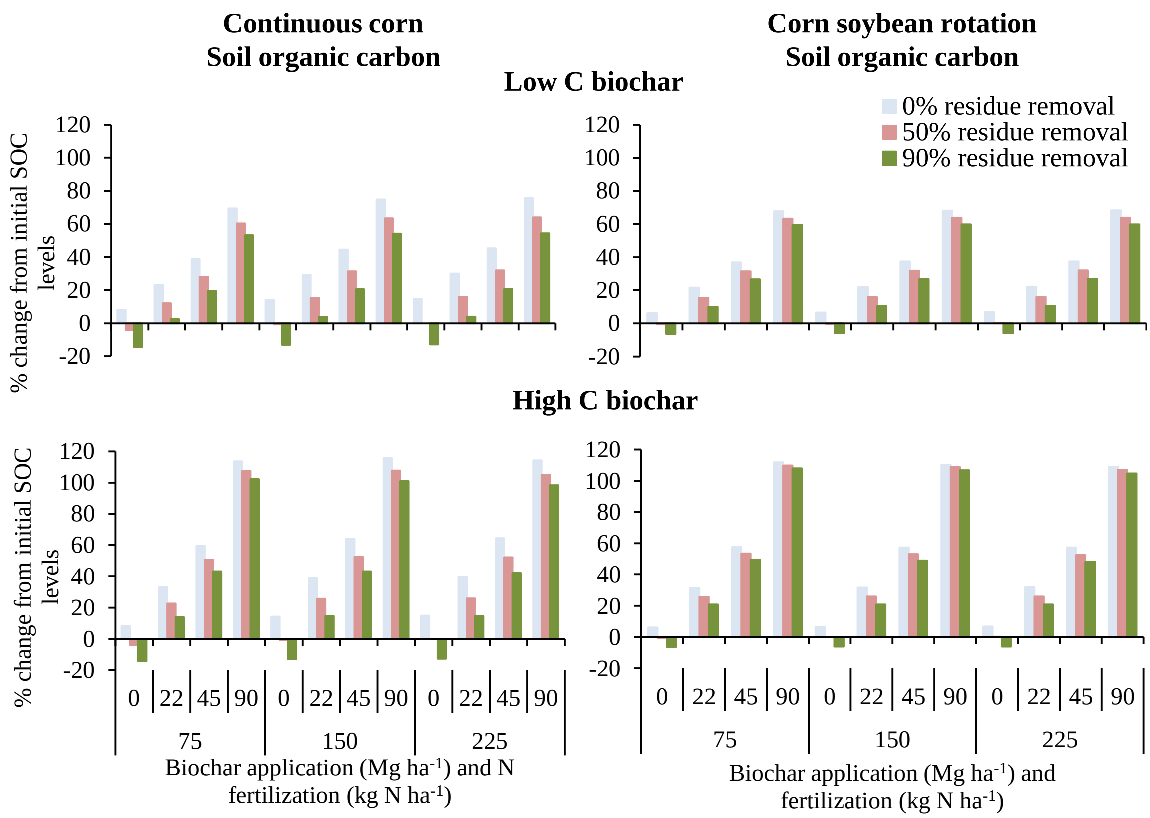

Fig. 8. Average change in total soil organic carbon levels for the 32 year simulation (1985-2016) in CC and CS rotation systems under different N fertilization and residue management scenarios and when low/high C content and C:N ratio biochars were applied in 1985.

Model application - Cost-Benefit Analysis

Results of the cost-benefit analysis indicate that sufficient nitrogen is needed to ensure a positive net benefit from biochar application. If there is a lack of nitrogen a significant yield drag results when biochar is applied (Tables S5, S6, and S7). The assessment of private benefits indicated that as residue removal rates increase the revenue from the corn crop decreases while that from the stover increases, with an overall increase in the net private benefits (Tables S5, S6, and S7). Further, biochar application rate is not linked to residue removal rate but it does impact corn yields. When no residue is removed the revenue from higher corn yields increases as biochar application rate increases, while at the higher residue removal rates corn revenue is negative relative to the baseline, but as biochar application rate increases the value becomes less negative (Tables S5, S6, and S7). Also, the net private benefits are boosted significantly as residue removal rate increases due to a higher value from the sale of corn stover, which at the same time diminishes the value of crop yield enhancements.

Our results reveal that the public benefits of biochar application, when coupled with the ability to harvest more crop residue, significantly outweigh the private benefits enjoyed by the farmer (Fig. 9). Further, the public benefits that result from lower CO_2 emissions are closely tied to biochar application rate, suggesting that an increase in biochar application rate from 22 to 90 Mg ha^{-1} would result in a proportional increase in aggregate SOC benefits. However, the marginal benefit of reducing CO_2 emissions due to additional biochar applied is stagnant or lower, or in other words, a higher biochar application rate actually causes a lower maximum price a farmer could afford to pay for biochar. In contrast, while a higher biochar application rate leads to a greater reduction in NO_3 leaching; the reduction in NO_3 leaching is also significantly enhanced with a higher residue removal rate. Actually, at 50 or 90% residue removal rate, the public benefits from the reduction in NO_3 leaching are substantially higher than the benefits that result from avoided CO_2 emissions (Tables S5, S6, and S7).

The breakeven price, both public and private, for farmers applying biochar increases as residue removal rates increase and decreases as biochar application rates increase for both cropping systems and high and low C and C:N ratio biochars. Lastly, results show that a high C and C:N ratio biochar results in greater benefits then a low C and C:N ratio biochar across all scenarios (Fig. 9 and Tables S5, S6, and S7).

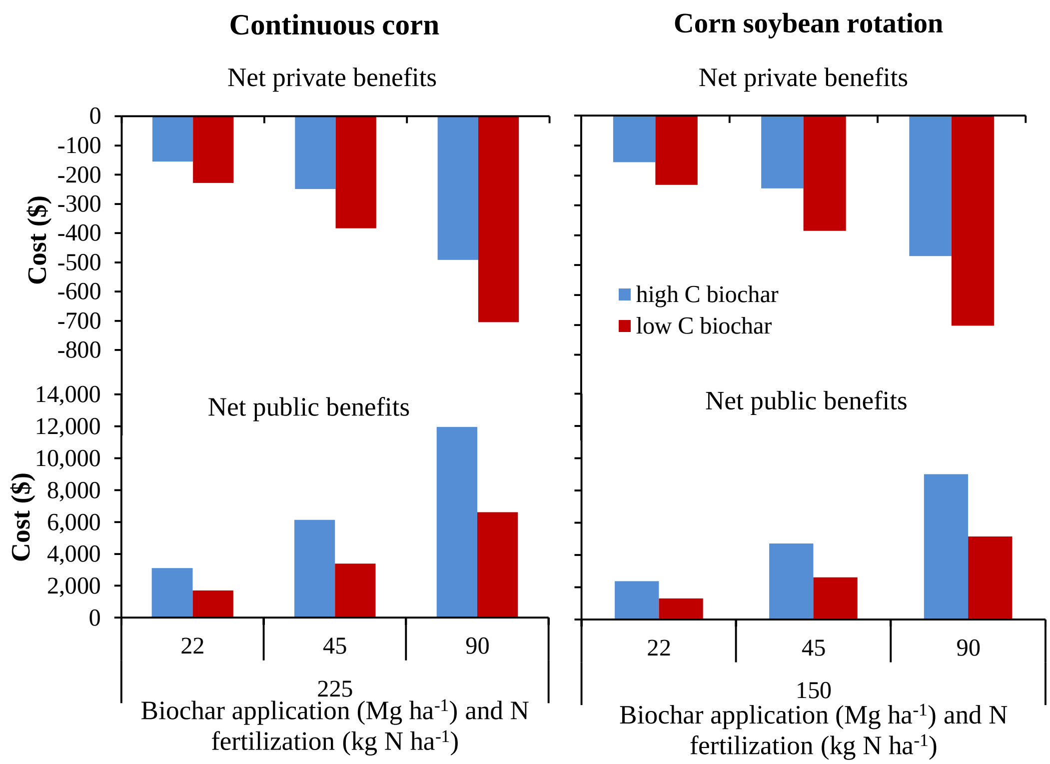

Fig. 9. Net private and net public benefits for the CC and the CS rotation systems for different biochar application rates, 0% residue removal, and when a high C biochar (blue bars) and low C biochar (red bars) is applied. Values are relative to the baseline scenarios of no biochar, 0% residue removal, and 225 kg N ha^{-1} and 150 kg N ha^{-1} for the CC and the CS rotation systems, respectively.

Discussion

Model Performance

This study calibrated the APSIM biochar model for a new site in central Iowa and used the calibrated model to identify the optimum biochar application rate that maximizes productivity and environmental performance of CC and CS cropping systems under different N fertilization rates and residue harvesting scenarios. Overall, the calibrated model performed well in predicting corn yields and satisfactory in predicting SOC levels for both the CC and CS rotation systems. The model was better at estimating corn yields and associated variability than SOC levels and associated variability.

Regarding corn yields, the decrease in the relative error of the model and the change in ME from a negative to positive value between the uncalibrated and calibrated models indicates a significant improvement in overall model performance. In particular, a ME value less than zero suggests that that model predictions are worse than the average of all observations (Wallach, 2006). Modifying a number of the soil profile, biochar, and management parameter settings during model initialization as well as several of the corn crop cultivar parameters during model calibration were important steps to achieving the good overall model fit.

The biochar model generally overestimated SOC, both on average (Fig. 4) and at the individual plot level (Fig. 5). This may be the result of the soil profile parameters having been calculated as the average across all replications and years measurements were taken and the biochar plots being excluded from the calculation.

The model response to the biochar applications used in this study is an immediate increase of 0.5% in SOC. This increase is due to the biochar application rate and the C content of the biochar. Over time after the biochar application the C:N ratio of the biochar and the relative size and residence time of the labile and recalcitrant biochar pools influences the biochar C decomposition rate. The biochar used during model calibration was a high carbon hardwood biochar (76% C) that also had a high C:N ratio of 232:1. Thus, the immediate increase in the predicted SOC values was not surprising. The rate of increase and the duration of the higher SOC levels predicted by the model will change if a low carbon biochar is used. This is why it was important to consider the impacts of applying two different types of biochar on yield and environmental impacts during model application. Moreover, the priming coefficient, which models biochars effect on altering turnover rates of SOC, was set to zero. However, if the priming coefficient was positive the application of biochar would have accelerated mineralization of the native soil OM and SOC levels would be lower than the observed value. By contrast, if the priming coefficient was negative the application of biochar would have reduced mineralization of the native soil OM and SOC levels would be higher than what was observed. This highlights the need for more research on biochars effect on priming.

Model Application

The long-term APSIM simulations revealed similar results for impacts of different management scenarios on corn yields, NO_3 leaching, and SOC content in both cropping systems and for the two different biochar types. The negligible change in corn yields and the trend observed as N fertilization rate increased were expected. The variable effects of biochar applications on corn yields in field studies have been widely reported on (Major et al., 2010: Uzoma et al., 2011; Cornelissen et al., 2013; Rogovska et al., 2016). Increasing the application rate of biochar may increase yield but a maximum may be reached, while similarly negative yield effects can be seen when the biochar application rate is too high. Whether the effect of biochar is positive or negative is environment, climate, and soil type dependent and other scenarios are likely to indicate different results.

One current limitation of the APSIM biochar model is that it does not yet incorporate the effects of allelopathy on corn yield predictions. Allelopathic compounds are released from decomposing crop residues and can have harmful carryover effects. Because of allelopathy, the presence of high residue loads from the previous year can decrease early seedling growth resulting in decreased crop yields in continuous corn systems (Rogovska et al., 2014; 2016). Removing some or all of the surface residue can improve yields by reducing the release of allelopathic compounds. At the same time, in scenarios where residues are left on the field and biochar is applied, corn yields have been found to increase from 0.8 – 3.8 Mg ha^{-1} depending on biochar application rate, due to the adsorption and deactivation of allelopathic compounds onto biochar surfaces (Rogovska et al., 2014; 2016). Thus, in the scenarios evaluated here the potential positive impacts on corn yields, in response to residue removal and biochar applications, were not considered. The inclusion of algorithms that account for allelopathic effects and the potential reduction in the harmful effects of allelopathic compounds due to biochar additions should be considered as future APSIM development work. This has the potential to improve yield predictions from APSIM in general and to better predict biochar impacts on crop yields. However, in addition to allelopathy, crop yields may be negatively impacted by large amounts of residue due to the presence of pests and pathogens, cold and wet soils in the spring, and N immobilization; factors that cannot be ignored when interpreting the results of this study.

The observation that residue removal decreases NO_3 leaching for the two lower N fertilization rates (75 and 150 kg N ha^{-1}) but increases NO_3 leaching for the higher fertilization rate (225 kg N ha^{-1}) (Fig. 7) is attributed to the combined effects of the biochars C:N ratio and the amount of residue remaining. When a biochar with a high C:N ratio is applied and there is greater residue left on the field, N immobilization limits NO_3 leaching (Fig. 7). When N fertilizer is already limiting, in the case of the 75 and 150 kg N ha^{-1} rate scenarios, and more residue is removed, a smaller fraction of N is immobilized. This lower rate of N immobilization means more is available to the plant and for root growth, which uptake more N and minimize NO_3 leaching rates. However, when N is in excess (225 kg N ha^{-1} rate scenario), and more residue remains, a greater fraction of N is immobilized and thus NO_3 leaching is reduced. When the biochar applied has a low C content and C:N ratio the effects on N immobilization are significantly lower (Fig. 7). The results of these scenario simulations highlight the importance of evaluating biochar quality. Different biochars impact agricultural systems and the environment differently and thus need to be produced and applied for specific end-uses (Spokas et al., 2012; Novak and Busscher, 2012; Ippolito et al., 2012).

Economic Trade-offs

The cost-benefits analysis suggests that if a farmer could use the per-ton breakeven price in a given scenario they could afford to pay for biochar, as it represents a crude measure of the cost-effectiveness of applying biochar. Comparing across various management scenarios revealed that private benefits alone, under current prevailing management practices that includes no residue removal, it is difficult to justify the procurement and application of biochar application. However, the APSIM model simulations and therefore this cost-benefit analysis do not consider the potential negative effects of high residue levels on crop yields, which may have significant negative economic implications. But for the present analysis the situation becomes more economically viable if a greater amount of residue can be removed, or if a farmer could be compensated via cost-shares or environmental trading schemes for the public benefits accrued from applying biochar (decreased NO_3 leaching and CO_2 emitted). In the 36 difference scenarios evaluated here we showed that a lower biochar application rate, 22 Mg ha^{-1} (10 T ac^{-1}), tends to yield higher per-ton benefits and a higher per-ton breakeven price the farmer would be able to pay for biochar. For example, a farmer can afford to pay $40 per ton for biochar, based on the private gains resulting from higher yields, they can harvest 50% of the residue and apply biochar at a rate of 22 Mg ha^{-1}.

Across all scenarios the application of biochar appeared to be more beneficial in the CC system compared to the CS rotation system, which may be linked to a lower nitrogen application rate in the CS rotation system due to soybeans ability to fix nitrogen, and thus have less NO_3 leached from the system. Under prevailing nitrogen application rates in central Iowa a yield drag is unlikely with biochar applications, however, a higher initial nitrogen application rate immediately after biochar application is recommended.

The private benefits were predominantly driven by yield gains, which tended to be overshadowed by the potential public benefits that would result from increasing SOC levels and reducing NO_3 leaching rates. However, the private benefits alone were not sufficient to guarantee a net private return from biochar application, as implied by the negative per-ton price if only private yield benefits were considered and there was no corn stover removal. Further, while an increase in biochar application rate, holding other things constant, would increase the total private and public benefits, the per-ton maximum price a farmer could pay for the biochar may not necessarily increase. Lastly, the greater the residue removal rate the more cost-effective the scenario was because there is a high value associated with selling the residue and greater reduction in NO_3 leaching rates. Thus residue can be removed sustainably if biochar carbon is added back to the soil, with positive benefits for both the farmer and society.

Conclusions

The findings from this study demonstrated that over a 32-year period biochar applications can eliminate negative effects of residue harvesting on soil quality while at the same time reducing nitrate leaching, increasing soil organic carbon, and not impacting corn yields. The simulations revealed that corn yields are most affected by the amount of N applied and not by the addition of biochar or residue removed. The opposite was true for NO_3 leaching, with increasing rates of biochar leading to the greatest reduction in nitrogen lost from the system. Biochar applications also resulted in the building of soil organic carbon even under increasing rates of residue removal. This finding in particular, could have important positive implications for the US bioenergy industry while improving the sustainability of our agricultural systems. The cost-benefit analysis revealed that the public benefits that result from applying biochar coupled with the ability to harvest more residue, significantly outweighed the private benefits. Biochar applications are an economically viable option in Iowa when at least 50% of the residue is harvested for sale; which can be done in an environmentally sustainable way. Future work in APSIM should consider factors that may negatively affect corn yields at high residue levels (e.g. allelopathy), potentially increasing the net private benefits associated with biochar applications.

Acknowledgments

This project is supported in part by the Global Climate and Energy Project, Stanford Subaward Agreement No. 60413992-112883-A, the National Science Foundation under Grant Number EPS-1101284, the USDA-NIFA Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30411, and the USDA-NIFA Hatch project No. IOW03814.

References

Aller, D., Mazur, R., Moore, K., Hintz, R., Laird, D., Horton, R., 2017. Biochar age and crop rotation impacts on soil quality. *Soil Sci Soc Am J.* doi:10.2136/sssaj2017.01.0010

Archontoulis, S.V., Miguez, F.E., Moore, K.J., 2014a. Evaluating APSIM maize, soil water, soil nitrogen, manure, and soil temperature modules in the Midwestern United States. Agron. J. 106, 1025–1040.

Archontoulis, S.V., Miguez, F.E., Moore, K.J., 2014b. A methodology and an optimization tool to calibrate phenology of short-day species included in the APSIM PLANT model: application to soybean. Environ. Modell. Softw. 62, 465–477.

Archontoulis, S.V., Miguez, F.E., 2015. Nonlinear regression models and applications in agricultural research. Agronomy Journal, 107, 786–798.

Archontoulis, S.V., Huber, I., Miguez, F.E., Thorburn, P.J., Rogovska, N., Laird, D.A., 2016. A model for mechanistic and system assessments of biochar effects on soils and crops and trade-offs. GCB Bioenergy 8, 1028–1045.

Basche, A.D., Archontoulis, S.V., Kaspar, T.C., Jaynes, D.B., Parkin, T.B., Miguez, F.E., 2016. Simulating long-term impacts of cover crops and climate change on crop production and environmental outcomes in the Midwestern United States. Agric. Ecosyst. Environ. 218, 95–106.

Blanco-Canqui, H., Lal, R., 2009. Crop residue removal impacts on soil productivity and environmental quality. Crit. Rev. Plant Sci. 28, 139-163. doi:10.1080/07352680902776507

Calkins, P.H., Dipietre, D.D., 1983. Farm business management: Successful decisions in a changing environment. MacMillan and Company, New York.

Cornelissen, G., Martinsen, V., Shitumbanuma, V., Alling, V., Breedveld, G., Rutherford, D., Sparrevik, M., Hale, S., Obia, A., Mulder, J., 2013. Biochar effect on maize yield and soil characteristics in five conservation farming sites in Zambia. Agronomy, 3, 256–274. doi:10.3390/agronomy3020256

Davis, A., Hill, J., Chase, C., Johanns, A., Liebman, M., 2012. Increasing cropping system diversity balances productivity, profitability and environmental health. PLoS ONE. 7:e47149. doi:10.1371/journal.pone.0047149

Dietzel, R., Liebman, M., Ewing, R., Helmers, M., Horton, R., Jarchow, M., Archontoulis, S., 2016. How efficiently do corn-and soybean-based cropping systems use water? A systems modeling analysis. Global Change Biol. 22, 666–681.

Edwards, W., 2014. Estimating a Value for Corn Stover. Iowa State University Extension and Outreach. https://www.extension.iastate.edu/agdm/crops/html/a1-70.html. Accessed 1 July 2017.

Food and Agricultural Organization of the United Nations (FAO)., 2014. The Water-Energy-Food Nexus: A new approach in support of food security and sustainable agriculture Food. http://www.fao.org/policy-support/resources/resources-details/en/c/421718/.

Food and Agriculture Organization of the United Nations FAOSTAT., 2015. (FAO, Rome). Available at faostat.fao.org/

Giller, K., M. Beare, P. Lavelle, A. Izac, and M. Swift., 1997. Agricultural intensification, soil biodiversity and agroecosystem function. Appl. Soil Ecol. 6, 3-16. doi:10.1016/S0929-1393(96)00149-7

He, D., Wang, E., Wang, J., Robertson, M., 2017. Data requirement for effective calibration of process-based crop models. Agr. Forest Meteorol. 234-235, 136-148. dx.doi.org/10.1016/j.agrformet.2016.12.015

Holzworth, D.P., Huth, N.I., deVoil, P.G., Zurcher, E.J., Herrmann, N.I., McLean, G., Chenu, K., van Oosterom, E.J., Snow, V.O., Murphy, C., Moore, A.D., Brown, H., Whish, J.P.M., Verrall, S., Fainges, J., Bell, L.W., Peake, A.S., Poulton, P.L., Hochman, Z., Thorburn, P.J., Gaydon, D.S., Dalgliesh, N., Rodriguez, D., Cox, H., Chapman, S., Doherty, A., Teixeira, E., Sharp, J., Cichota, R., Vogeler, I., Li, F.Y., Wang, E., Hammer, G.L., Robertson, M.J., Dimes, J.P., Whitbread, A.M., Hunt, J., van Rees, H., McClelland, T., Carberry, P.S., Hargreaves, J.N.G., MacLeod, N.D., McDonald, C.K., Harsdorf, J., Wedgwood, S., Keating, B.A., 2014. APSIM - evolution towards a new generation of agricultural systems simulation. Environ. Modell. Softw. 62, 327-350. doi.org/10.1016/j.envsoft.2014.07.009

Iowa Environmental Mesonet. *Iowa Ag Climate Network*. Ames, IA: Iowa State University. Available at: http://mesonet.agron.iastate.edu/agclimate/ (accessed 15 February 2017).

Ippolito, J.A., Laird, D.A., Busscher, W.J., 2012. Environmental Benefits of Biochar. J. Environ. Qual. 41. doi:10.2134/jeq2012.0151

Johanns, A.J., 2017. Cash Corn and Soybean Prices**.** Iowa State University Extension and Outreach. https://www.extension.iastate.edu/agdm/crops/html/a2-11.html. Accessed 1 July 2017.

Karlen, D.L., Hurley, E.G., Andrews, S.S., Cambardella, C.A., Meek, D.W., Duffy, M.D., Mallarino, A.P., 2006. Crop rotation effects on soil quality at three northern corn/soybean belt locations. Agron. J. 98, 484–495. doi:10.2134/agronj2005.0098

Keating, B.A., Carberry, P.S., Hammer, G.L., Probert, M.E., Robertson, M.J., Holzworth, D., Huth, N. I., Hargreaves, J.N.G., Meinke, H., Hochman, Z., McLean, G., Verburg, K., Snow, V., Dimes, J.P., Silburn, M., Wang, E., Brown, S., Bristow, K.L., Asseng, S., Chapman, S., McCown, R.L., Freebairn, D.M., Smith, C.J., 2003. An overview of APSIM, a model designed for farming systems simulation. European Journal of Agronomy 18, 267- 288.

Laird, D.A., Brown, R.C., Amonette, J.E., Lehmann, J., 2009. Review of the pyrolysis platform for coproducing bio-oil and biochar. Biofuels Bioproducts Biorefining. 3, 547-562.

Laird, D.A., Chang, C-W., 2013. Long-term impacts of residue harvesting on soil quality. Soil Tillage Res. 134, 33-40. doi.org/10.1016/j.still.2013.07.001

Lal, R., 2015. A system approach to conservation agriculture. J. Soil Water Conserv. 70, 82A-88A. doi:10.2489/jswc.70.4.82A

Lal, R., Pimentel, D., 2007. Biofuels from crop residues. Soil Tillage Res. 93, 237-238.

Lehmann, J., Joseph, S., 2015. Biochar for environmental management: science, technology and implementation. Taylor and Francis, London.

Liebman, M., Helmers, M., Schulte, L., Chase. C., 2013. Using biodiversity to link agricultural productivity with environmental quality: Results from three field experiments in Iowa. Renew. Agr. Food Syst. 28, 115-128. doi:10.1017/S1742170512000300

Major, J., Rondon, M., Molina, D., Riha, S., Lehmann, J., 2010. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna Oxisol. Plant Soil. 333:117-128. doi.10.1007/s11104-010-0327-0

Malone, R., Huth, N., Carberry, P., Ma, L., Kaspar, T., Karlen, D., Meade, T., Kanwar, R., Heilman, P., 2007. Evaluating and predicting agricultural management effects under tile drainage using modified APSIM. Geoderma 140, 310-322.

Martinez-Feria, R.A., Dietzel, R., Liebman, M., Helmers, M.J., Archontoulis, S.V., 2016. Rye cover crop effects on maize: a system-level analysis. Field Crops Res. 196, 145-159.

Newton, J., Kuethe, T., 2015. Changing landscape of corn and soybean production and potential implications in 2015, Farm doc Daily. Dept of Agricultural and Consumer Economics, University of Illinois, Urbana-Champaign, IL.

Nordhaus, W.D., 2017. Revisiting the social cost of carbon. PNAS. 114(7): 1518-1523. doi: 10.1073/pnas.1609244114

Novak, J.M., Busscher, W.J., 2012. Selection and use of designer biochars to improve characteristics of southeastern USA Coastal Plain degraded soils. In: J.E. Lee, editor, Advanced biofuels and bioproducts. Springer Science, New York (in press). doi:10.1007/978-1-4614-3348-4-7.

Ojeda, J., Volenec, J Brouder, S Caviglia, O., Agnusdei, M., 2017. Evaluation of agricultural production systems simulator as yield predictor of Panicum virgatum and Miscanthus x giganteus in several US environments. GCB Bioenergy 9, 796-816. doi:10.1111/gcbb.12384

Perlack, R.D., Wright, L.L., Turhollow, A.F., Graham, R.L., Stokes, B.J., Erbach, D.C., 2005. Biomass as feedstock for a bioenergy and bioproducts industry: The technical feasibility of a billion-ton annual supply. DOE/USDA Tech. Rep. DOE/GO-102005–2135 ORNL/TM-2005/66. www.ornl.gov/~webworks/cppr/y2001/rpt/123021.pdf[verified 23 Oct. 2007]. USDOE, Office of Scientific & Technical Information, Oak Ridge, TN.

Probert, M.E., Dimes, J.P., Keating, B.A., Dalal, R.C., Strong, W.M., 1998. APSIM's water and nitrogen modules and simulation of the dynamics of water and nitrogen in fallow systems. Agric. Syst. 56, 1-28. doi: 10.1016/S0308-521X(97)00028-0

Ribaudo, M., Savage, J., Aillery, M., 2014. An economic assessment of policy options to reduce agricultural pollutants in the Chesapeake Bay. ERR-166. U.S. Department of Agriculture, Economic Research Service.

Rogovska, N., Laird, D.A., Rathke, S.J., Karlen, D.L., 2014. Biochar impact on Midwestern Mollisols and maize nutrient availability. Geoderma 230, 340-347. doi.org/10.1016/j.geoderma.2014.04.009

Rogovska, N., Laird, D.A., Karlen, D.L., 2016. Corn and soil response to biochar application and stover harvest. Field Crops Res. 187, 96-106. doi.org/10.1016/j.fcr.2015.12.013

Russell, A.E., Laird, D.A., Mallarino, A.P., 2006. Impact of Nitrogen Fertilization and Cropping System on Soil Quality in Midwestern Mollisols. Soil Sci. Soc. Am. J. 70:249-255.

Spokas, K.A., Cantrell, K.B., Novak, J.M., Archer, D.A., Ippolito, J.A., Collins, H.P., Boateng, A.A., Lima, I.M., Lamb, M.C., McAloon, A.J., Lentz, R.D., Nichols., K.A., 2012. Biochar: A synthesis of its agronomic impact beyond carbon sequestration. J. Environ. Qual. 41, 973-989. doi:10.2134/jeq2011.0069

Thorburn, P.J., Probert, M.E., Robertson, F.A., 2001. Modelling decomposition of sugarcane surface residues with APSIM-Residue. Field Crops Res. 70, 223-232. doi:10.1016/S0378-4290(01)00141-1

Thorburn, P.J., Meier, E.A., Probert, M.E., 2005. Modelling nitrogen dynamics in sugarcane systems: recent advances and applications. Field Crops Res. 92, 337-352. doi:10.1016/j.fcr.2005.01.016

USDA-NASS 2016. Quick-Stats. https://www.nass.usda.gov/Quick_Stats/Ag_Overview/stateOverview.php?state=IOWA (4.12.16.).

Uzoma, K. C., Inoue, M., Andry, H., Fujimaki, H., Zahoor, A., Nishihara, E., 2011. Effect of cow manure biochar on maize productivity under sandy soil condition. Soil Use and Management, 27, 205–212. doi:10.1111/j.1475-2743.2011.00340.x

Wallach, D., 2006. Evaluating crop models. In: D. Wallach et al., editors, Working with dynamic crop models: Evaluations, analysis, parameterization, and applications. Elsevier, Amsterdam. p. 11–53.

Wilhelm, W.W., Johnson, J.M.F., Hatfield, J.L., Voorhees, W.B., Linden, D.R., 2004. Crop and soil productivity response to corn residue removal: A literature review. Agron. J. 96(1), 1-17.

Wilhelm, W.W., Johnson, J.M.F., Karlen, D., Lightle, D., 2007. Corn stover to sustain soil organic carbon further constrains biomass supply. Agron. J. 99, 1665-1667. doi:10.2134/agronj2007.0150

Appendix - supplementary data

Table S1. Soil water profile parameters used in model calibration and application for both the continuous corn and corn-soybean rotation systems. Key: bulk density (BD), air dry limit (AirDry), water content at 15 bar (LL), water content at 1/3 bar (DUL), saturation point (SAT), saturated hydraulic conductivity (KS), plant available water capacity (PAWC), maximum root water extraction rate (KL), and constraints to root growth (XF; 1 = no constraint to growth).

Depth (cm)	BD (g cc^{-1})	AirDry (mm mm^{-1})	LL15 (mm mm^{-1})	DUL (mm mm^{-1})	SAT (mm mm^{-1})	KS (mm day^{-1})	Maize/Soy LL	Maize/Soy PAWC	Maize/Soy KL	Maize/Soy XF
0-5	1.276	0.099	0.163	0.321	0.596	296.00	0.163	7.9	0.08	1.0
5-15	1.434	0.109	0.173	0.329	0.564	296.00	0.173	15.6	0.08	1.0
15-30	1.271	0.098	0.179	0.349	0.630	235.00	0.179	25.5	0.08	1.0
30-50	1.244	0.167	0.167	0.328	0.611	171.00	0.167	32.2	0.08	1.0
50-75	1.346	0.157	0.157	0.316	0.601	143.00	0.157	39.8	0.05	1.0
75-100	1.346	0.157	0.157	0.316	0.601	129.00	0.157	39.8	0.05	1.0
100-140	1.346	0.157	0.157	0.316	0.601	129.00	0.157	63.6	0.03	1.0
140-180	1.346	0.157	0.157	0.316	0.601	129.00	0.157	63.6	0.01	1.0
180-220	1.346	0.157	0.157	0.316	0.601	129.00	0.157	0.0	0.01	0.0

Table S2. Soil organic matter profile parameters used on 1/1/2000 for model calibration and 1/1/1980 for model application of both the continuous corn and corn-soybean rotation systems. Key: soil organic carbon (OC), fraction of carbon in biom pool (FBiom), fraction of inert carbon (FInert).

Depth (cm)	OC (total %)	FBiom (0-1)	FInert (0-1)
0-5	2.229	0.100	0.400
5-15	2.174	0.090	0.400
15-30	2.264	0.080	0.574
30-50	1.561	0.070	0.800
50-75	1.324	0.060	0.810
75-100	1.324	0.030	0.850
100-140	0.500	0.030	0.880
140-180	0.400	0.010	0.890
180-220	0.300	0.010	0.910

Table S3. Biochar parameters used for both the continuous corn and corn-soybean rotation systems. During model initialization and calibration 'date of biochar application' was variable depending on experimental data (05/14/2012, 05/08/2013, 05/10/2014). During model application 'date of biochar application' was fixed at 05/08/1985, while 'amount of biochar applied (kg/ha)' changed depending on the scenario (0, 22417, 44833, 89666).

Description	Value (High C biochar)	Value (Low C biochar)
Date of biochar application (mm/dd/yyyy)	05/08/1985, 05/14/2012 - 5/10/2014	05/08/1985
amount of biochar applied (kg/ha)	22417 - 89666	22417 - 89666
fraction carbon in biochar (0-1)	0.76	0.46
fraction of biochar lost during application (0-1)	0.02	0.02
mean residence time for labile biochar pool (years)	1	1
mean residence time for resistant biochar pool (years)	500	500
biochar labile fraction (0-1)	0.13	0.11
fraction of decomposed biochar that goes to OC pools (0-1) (biochar efficiency)	0.4	0.4
fraction of decomposed biochar that goes to biom (0-1)	0.05	0.05
biochar CN ratio	232	76
sand (0-1)	0.46	0.46
clay (0-1)	0.24	0.24
priming coefficient for biom pool (-1 to 1) use 0.05	0	0
priming coefficient for hum pool (-1 to 1) use 0.05	0	0
priming coefficient for cell pool (-1 to 1) use 0.08	0	0
priming coefficient for carb pool (-1 to 1) use 0.08	0	0
priming coefficient for lign pool (-1 to 1) use 0.08	0	0
negative priming coefficient for internal C partitioning (use 0.1 for 20 Mg), biom	0	0
negative priming coefficient for internal C partioning (use -0.1), biom	0	0
negative priming for internal C partitioning (use 0.1 for 20 mg),fom	0	0
negative priming for internal C partitioning (use -0.1 for 20 mg), fom	0	0
C/N ratio of biom pool:	8	8
C/N ratio of soil stuff:	12	12
Biochar incorporation depth (mm):	200	200
Slope of dul quality equation (default 0.33)	0.15	0.15
Slope of bd quality equation (default 0.33)	0.15	0.15
Biochar LV (cmol/kg?)	50	50
Biochar ECEC (cmol/kg)	187	187
Biochar cnrf coefficient (0-1)	0.693	0.693
Optimum cn ratio for bc	25	25
Biochar WFPS factor (0-1)	1	1
Biochar nh4 absorption coefficient (Langmuir)	0.006	0.006
Biochar nh4 desorption coefficient (Langmuir)	0.006	0.006

Table S4. Changes made to the B_110 maize cultivar during model calibration. Units of growing degree days (GDD).

Description	**Original value**	**Updated value**
Emergence to end of juvenile (GDD)	214	250
Flowering to maturity (GDD)	885	820
Flowering to start of grain fill (GDD)	150	170
Maturity to ripening (GDD)	1	180

Table S5. Results of the cost-benefit analysis when biochar application rate changes and no residue is removed. Values are relative to the baseline scenarios of 225 kg N ha^{-1} and 150 kg N ha^{-1} for the CC and the CS rotation systems, respectively, with no residue removal, and no biochar.

Management					Private benefits			Public benefits			Breakeven costs	
Cropping system	Biochar C:N ratio	Biochar application rate (Mg ha^{-1})	Nitrogen application rate (kg ha^{-1})	Residue removal rate (%)	Revenue change in corn yields ($)	Revenue change from stover removal ($)	Net private benefits ($)	Benefit of reduced NO_3-N leaching ($)	Benefit of increasing SOC levels ($)	Net public benefit ($)	Private breakeven costs ($)	Public breakeven costs ($)
Continuous Corn	High	0	225	0	0.00	0.00	0.00	0.00	0.00	0.00		
		22	225	0	201.58	0.00	-155.42	1,473.26	1,643.24	3,116.50	-2.57	51.51
		45	225	0	376.64	0.00	-249.46	2,846.90	3,291.75	6,138.65	-2.02	49.61
		90	225	0	660.93	0.00	-491.67	5,352.79	6,601.97	11,954.76	-1.99	48.30
	Low	0	225	0	0.00	0.00	0.00	0.00	0.00	0.00		
		22	225	0	128.48	0.00	-228.52	720.35	995.43	1,715.77	-3.78	28.36
		45	225	0	242.81	0.00	-383.29	1,400.46	1,990.85	3,391.31	-3.10	27.40
		90	225	0	447.82	0.00	-704.78	2,639.99	3,981.74	6,621.73	-2.85	26.75
Corn-Soybean	High	0	150	0	0.00	0.00	0.00	0.00	0.00	0.00		
		22	150	0	201.65	0.00	-155.35	714.60	1,653.78	2,368.38	-2.57	39.15
		45	150	0	383.45	0.00	-242.65	1,383.22	3,315.45	4,698.67	-1.96	37.97
		90	150	0	683.39	0.00	-469.21	2,362.20	6,636.17	8,998.37	-1.90	36.36
	Low	0	150	0	0.00	0.00	0.00	0.00	0.00	0.00		
		22	150	0	125.93	0.00	-231.07	316.11	995.43	1,311.54	-3.82	21.68
		45	150	0	240.71	0.00	-385.39	607.31	1,996.12	2,603.43	-3.11	21.04
		90	150	0	450.40	0.00	-702.20	1,151.41	3,994.87	5,146.27	-2.84	20.79

Table S6. Results of the cost-benefit analysis when biochar application rate changes and 50% of the residue is removed. Values are relative to the baseline scenario of 150 kg N ha^{-1}, no residue removal, and no biochar.

Management					Private benefits			Public benefits			Breakeven costs	
Cropping system	Biochar C:N ratio	Biochar application rate (Mg ha^{-1})	Nitrogen application rate (kg ha^{-1})	Residue removal rate (%)	Revenue change in corn yields ($)	Revenue change from stover removal ($)	Net private benefits ($)	Benefit of reduced NO_3-N leaching ($)	Benefit of increasing SOC levels ($)	Net public benefit ($)	Private breakeven costs ($)	Public breakeven costs ($)
Continuous Corn	High	0	225	50	-930.90	3,674.95	2,744.05	6,764.74	-316.01	6,448.73		
		22	225	50	-707.39	3,674.95	2,610.56	8,435.33	1,329.87	9,765.20	43.15	161.41
		45	225	50	-518.86	3,674.95	2,529.98	10,109.75	2,981.01	13,090.76	20.44	105.78
		90	225	50	-219.77	3,674.95	2,302.58	13,117.58	6,293.79	19,411.37	9.30	78.43
	Low	0	225	50	-930.90	3,674.95	2,744.05	6,764.74	-316.01	6,448.73		
		22	225	50	-787.65	3,674.95	2,530.30	7,550.23	679.42	8,229.64	41.82	136.03
		45	225	50	-663.29	3,674.95	2,385.55	8,306.97	1,677.48	9,984.45	19.28	80.68
		90	225	50	-445.73	3,674.95	2,076.61	9,736.17	3,668.33	13,404.50	8.39	54.16
Corn-Soybean	High	0	150	50	-883.67	3,674.95	2,791.28	5,703.38	-181.70	5,521.68		
		22	150	50	-732.25	3,674.95	2,585.70	6,255.14	1,464.17	7,719.31	42.74	127.59
		45	150	50	-603.36	3,674.95	2,445.48	6,690.03	3,123.21	9,813.24	19.76	79.30
		90	150	50	-417.03	3,674.95	2,105.31	7,188.14	6,438.66	13,626.80	8.51	55.06
	Low	0	150	50	-883.54	3,674.95	2,791.41	5,703.38	-181.70	5,521.68		
		22	150	50	-777.13	3,674.95	2,540.81	5,952.44	805.82	6,758.26	42.00	111.71
		45	150	50	-682.69	3,674.95	2,366.16	6,182.33	1,798.61	7,980.95	19.12	64.49
		90	150	50	-520.54	3,674.95	2,001.81	6,582.74	3,781.56	10,364.30	8.09	41.88

Table S7. Results of the cost-benefit analysis when biochar application rate changes and 90% of the residue is removed. Values are relative to the baseline scenario of 150 kg N ha^{-1}, no residue removal, and no biochar.

Management					Private benefits			Public benefits			Breakeven costs	
Cropping system	Biochar C:N ratio	Biochar application rate (Mg ha^{-1})	Nitrogen application rate (kg ha^{-1})	Residue removal rate (%)	Revenue change in corn yields ($)	Revenue change from stover removal ($)	Net private benefits ($)	Benefit of reduced NO_3-N leaching ($)	Benefit of increasing SOC levels ($)	Net public benefit ($)	Private breakeven costs ($)	Public breakeven costs ($)
Continuous Corn	High	0	225	90	-3,485.73	7,349.89	3,864.16	13,335.99	-589.88	12,746.10		
		22	225	90	-3,169.15	7,349.89	3,823.74	14,792.01	1,055.99	15,848.00	63.20	261.95
		45	225	90	-2,938.33	7,349.89	3,785.46	16,223.12	2,707.14	18,930.25	30.59	152.97
		90	225	90	-2,662.65	7,349.89	3,534.64	18,416.73	6,019.95	24,436.68	14.28	98.73
	Low	0	225	90	-3,485.73	7,349.89	3,864.16	13,335.99	-589.88	12,746.10		
		22	225	90	-3,287.14	7,349.89	3,705.75	14,033.34	405.54	14,438.89	61.25	238.66
		45	225	90	-3,107.18	7,349.89	3,616.62	14,703.88	1,400.97	16,104.85	29.23	130.14
		90	225	90	-2,828.95	7,349.89	3,368.34	15,901.26	3,397.09	19,298.35	13.61	77.97
Corn-Soybean	High	0	150	90	-2,911.66	7,349.89	4,438.23	8,130.72	-347.61	7,783.11		
		22	150	90	-2,920.85	7,349.89	4,072.05	8,452.58	1,298.27	9,750.84	67.31	161.17
		45	150	90	-2,977.91	7,349.89	3,745.88	8,686.31	2,957.31	11,643.61	30.27	94.09
		90	150	90	-3,030.98	7,349.89	3,166.31	8,979.42	6,270.13	15,249.55	12.79	61.61
	Low	0	150	90	-2,911.53	7,349.89	4,438.37	8,130.72	-347.61	7,783.11		
		22	150	90	-2,867.69	7,349.89	4,125.20	8,299.31	639.92	8,939.23	68.19	147.76
		45	150	90	-2,833.00	7,349.89	3,890.79	8,429.59	1,632.71	10,062.29	31.44	81.31
		90	150	90	-2,796.52	7,349.89	3,400.77	8,636.49	3,618.29	12,254.79	13.74	49.51

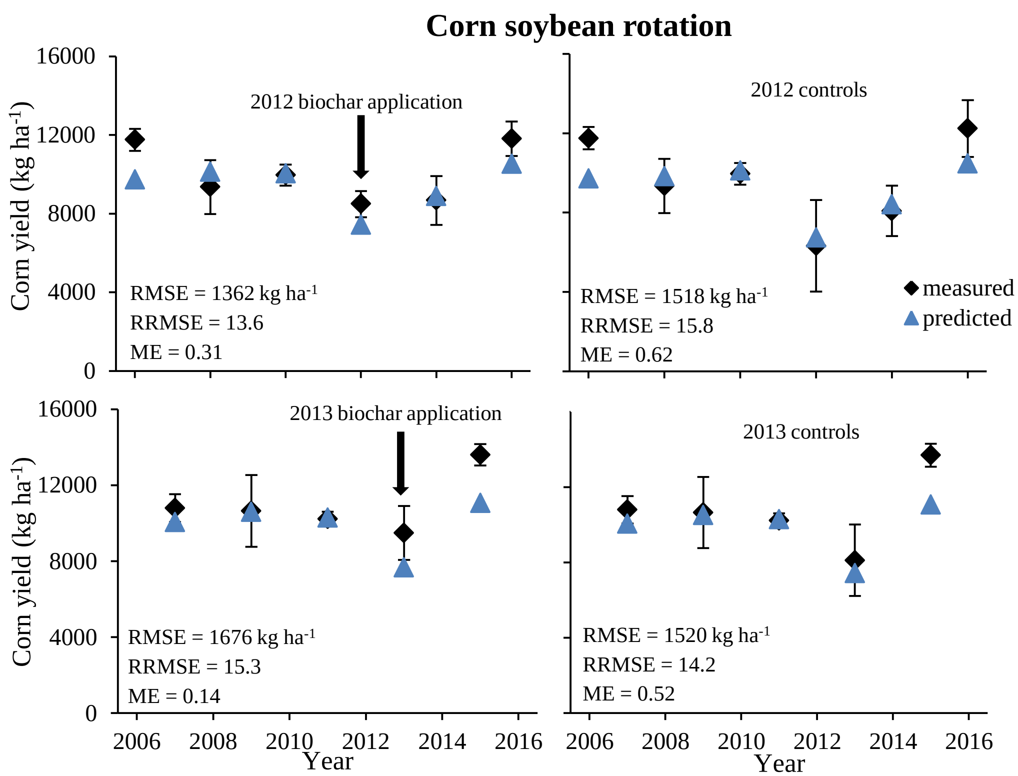

Fig. S1. Corn yields as impacted by two different field ages of biochar under CS rotation system (biochar applied in 2012 or 2013). Measured values (black diamonds) are the average of all plots with biochar (left side) and no-biochar control plots (right side) with standard deviation bars across all 11 years. Predicted yields are represented by the blue triangles.

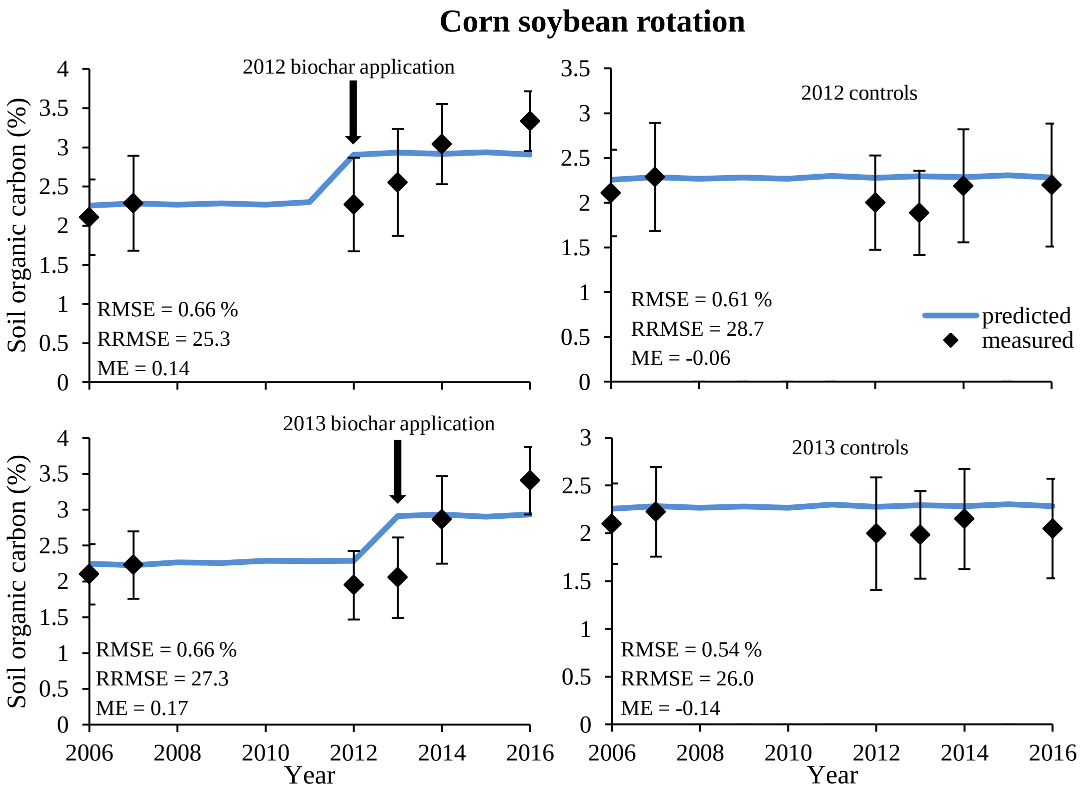

Fig. S2. Percent SOC across 11 years as impacted by two different field ages of biochar (biochar applied in 2012 or 2013) for the CS rotation system. Measured values (black diamonds) are the average of all plots with biochar (left side) and no-biochar control plots (right side) with bars showing standard deviations. Predicted yields are represented by the blue triangles.

CHAPTER 7. GENERAL CONCLUSIONS

Finding solutions to food-water-energy nexus challenges requires a systems approach and integration across scales to address issues of food production, environmental degradation, and energy consumption. Biochar has the potential to simultaneously address many of these issues by improving soil fertility, sequestering atmospheric C, and enhancing crop productivity. However, the majority of the positive benefits associated with biochar applications have been observed in studies using freshly produced biochars. These studies did not consider the changes that occur to biochar properties upon aging (weathering) in soil environments. Thus, the positive impacts of biochar observed in the short term may not be representative of its longer-term impacts on agronomic functions and environmental sustainability. Here a series of laboratory, greenhouse, field, and modeling studies were conducted to advance understanding of biochar and biochar aging impacts on soil physical and chemical properties, soil water relations, and crop productivity.

Prior to the studies included in this dissertation a rapid laboratory aging procedure for biochars was developed to improve understanding of how biochar properties change over time (biochar aging) (Bakshi et al., 2016). In that study the physical and chemical properties of 22 different biochars (11 fresh, 6 lab-aged, and 5 field-aged biochars) were characterized and compared. During characterization problems were found when the ASTM proximate analysis method (ASTM, 2007), originally developed for assessing quality of hardwood charcoal for use as fuel but has been widely used for biochars, was used to determine moisture, volatile matter (VM), fixed carbon (FC), and ash content of the 22 biochars. Specifically, during moisture content determination we found weight gain in biochars when heated at 105°C and during VM determination the heating of samples was inconsistent, only a limited number of samples could be analyzed at a single time, and there were safety concerns associated with moving samples around in a hot furnace. Therefore, we developed a modified proximate analysis method that addresses these problems, accounts for biochar property diversity, and is reliable for assessing biochar quality and stability in soils (Chapter 2).

In chapter 2, we showed that significant differences exist between the ASTM proximate analysis method and our Modified method. Results showed that a N_2 purge is necessary during both moisture and VM determination to avoid errors associated with sample oxidation, which are inherent to the ASTM method. Also, results revealed that when a range of boundary temperatures (350–950°C) were assessed, 800°C was determined to be the minimum temperature required to distinguish between VM and FC in biochars. Results overall showed that our Modified method was more appropriate for use in the proximate analysis of biochars to evaluate biochar quality and that VM/FC ratios are reliable for assessing the long-term stability of biochar C in soils. Lastly, the study showed that the Modified method can analyze a large number of samples simultaneously while reducing sample handling and potential hazards. Use of the Modified method by researchers across the biochar community will help minimize differences in study results, facilitate greater comparison of biochar properties between researchers, and provide reliable information about the long-term stability of different biochars in soil environments.

Utilizing an established long-term bioenergy cropping system experiment we investigated the effects of biochar, biochar age, and crop rotations, as well as their interactions, on a series of soil physical and chemical properties (Chapter 3). Following the collection of 208 intact soil cores and conducting a solute transport study, results showed that crop rotations that include switchgrass or triticale increase both retardation and dispersivity relative to continuous corn or corn-soybean rotations. Further, biochar amendments decrease dispersivity relative to no-biochar controls. Across the five cropping systems examined, there was an increase in total soil C and N, soil C/N ratio, pH and gravity drained water content, and a decrease in bulk density (BD) for soils treated with biochar relative to no-biochar controls. Continuous switchgrass stands were found to build soil C and N, increase retention of plant available P and K, and lower BD relative to the continuous corn system. Biochar age was found to have no effect on soil quality parameters measured in 2014 but significant increases with biochar age were found for total soil C and N in 2016. The difference in soil C and N levels between the 2014 and 2016 sampling suggested that biochar age is an important factor to consider in biochar studies that assess soil quality. Lastly, the significant interaction effects found between biochar and crop rotations emphasized the complexity of investigating soil quality responses to biochar amendments under different management strategies. Overall, the results indicate that biochar amendments and alternative crop rotations that include switchgrass help mitigate some of the adverse effects of biomass harvesting on soil quality and thus could contribute to enhancing the sustainability of bioenergy cropping systems in the Midwest.

Twenty-two biochars were used in the development of a modified proximate analysis method for biochars (Chapter 2). Of these 22 biochars, 12 (six fresh and six lab-aged) were used in a greenhouse study. This greenhouse study evaluated the influence of biochar age, biochar type, and their interaction on plant available water (PAW) and water use efficiency (WUE) in maize for three texturally diverse soils (Chapter 4). Results showed that aged biochars do not have the same impact on soil water relations as the equivalent fresh biochars. Specifically, both fresh and aged biochars increased soil moisture retention in a clay loam soil, had no impact in a silt loam soil, and had variable effects in a sandy loam soil. Fresh biochar increased final maize biomass weight in the sandy loam and silt loam soils and decreased final biomass weight in the clay loam soil, while aged biochar increased biomass weight in the silt loam soil. Both fresh and aged biochars decreased PAW in the clay loam soil and had no impact on PAW in the silt loam soil. Fresh biochar increased PAW, while aged biochar had no effect on PAW for the sandy loam soil. WUE decreased in response to both fresh and aged biochars in the clay loam soil and was variable for the other two soils. Overall, the influence of fresh and aged biochars on soil BD, soil water retention, PAW, WUE, and maize height and weight were highly variable and differed by biochar type; resulting in positive, negative, or neutral effects depending on soil type and the response variable. Furthermore, when the water drop penetration test (WDPT) was conducted to assess biochar water repellency, all aged biochars were more hydrophilic than their fresh counterparts and the relative degree of biochar hydrophobicity was further decreased after a drying-wetting-drying treatment. This study showed that biochar remains a promising tool to improve water management in rainfed agriculture, but biochar applications must be made strategically and take into account biochar type, soil type, and biochar age. Future work is needed to determine whether the results obtained from this greenhouse study are applicable in the field and over longer time scales.

The final two studies utilized a recently developed biochar model (Archontoulis et al., 2016) within the APSIM cropping systems model (Holzworth et al., 2014). The first of these studies (Chapter 5), showed that the pedotransfer functions (PTFs) of Saxton and Rawls (2006) and the soil parameters from the Web Soil Survey database provide the best estimates of soil water and physical parameters for topsoils with and without biochar compared to the PTFs developed by Gijsman et al. (2003) and Palmer et al. (2017). Further examination of the Saxton and Rawls (2006) PTFs against measured data for describing the relationship between PAW and

SOM, revealed no differences in the rate of change (slope) between biochar C and C in biogenic OM in these topsoils, but a difference in the magnitude of the response (intercept). For subsoils differences in both the rate and magnitude of change were found, indicating that the Saxton and Rawls (2006) PTFs underestimate PAW for a given SOM content and do not accurately describe the relationship between PAW and SOM in the subsoils analyzed. Furthermore, during APSIM biochar model calibration we found that model performance is improved when the modified Saxton and Rawls (2006) PTFs, which include quality modifiers to describe biochar impacts on soil water parameters, are used. But the quality modifiers were shown to be site-specific, with local calibration required to most accurately predict the impacts of biochar on soil water parameters. Results also indicated that tradeoffs exist for some parameter estimates (i.e. BD and SAT) when trying to optimize model performance because the estimate of one is dependent on the other. Lastly, model simulations revealed that in general as biochar application rates increase the lower limit (LL) increases but currently the model does not respond to changes in LL due to biochar. Therefore, future work is needed to determine whether model performance is improved when the quality modifier for LL (Q_{LL}) and hence model predictions of LL can change in response to biochar additions.

The second study utilizing the APSIM modeling platform as well as soil, crop yield, and management data from the long-term bioenergy cropping system study (Chapter 3), revealed that over a 32-year period biochar applications can eliminate negative effects associated with residue harvesting, as evaluated by reduced nitrate leaching rates and increased SOC levels, while not impacting corn yields (Chapter 6). Model simulations showed that nitrogen application rate is the strongest determinant of corn yields; with biochar applications and residue removal having a minimal effect. However, a direct relationship was found between increasing biochar application rates and decreasing nitrate leaching rates. Additionally, biochar applications increased SOC levels even under increasing residue removal rates. This finding was especially important because as more crop residues are harvested to support the growing US bioenergy industry, this residue can be removed sustainably if biochar is applied. The final component of this study was to employ a cost-benefit analysis to identify the economically optimal biochar application rate from both the private and public perspective. This analysis revealed that public benefits, as evaluated by a reduction in nitrate leaching rates and increased SOC levels, outweighed the private revenue gained from increased corn crop yields. Further, the lower the biochar application rate (i.e. 22 Mg ha^{-1}) the more cost-effective (per ton) applying biochar was determined to be. Overall, the application of biochar in central Iowa was found to be an economically viable option when at least 50% of the crop residue is harvested for sale, which can be done without negatively impacting soil and environmental quality over the long-term when biochar is subsequently applied. Further research, however, is needed in the APSIM biochar model to address factors other than N immobilization (e.g. allelopathy) which may negatively affect corn yields at high residue levels. Consideration of these factors in APSIM will likely influence the economics of biochar applications, potentially increasing the net private benefits from applying biochar.

In conclusion, the five studies included in this dissertation sought to advance understanding of the impacts of biochar and biochar aging on soil physical and chemical properties, soil water dynamics, and corn yield response in sustainable bioenergy cropping systems, through a series of systematically integrated studies across the laboratory, greenhouse, field, and modeling scales. Overall findings indicated that, biochar properties change over time, the appropriate methods must be used when working with biochars, and simple methods can be used to determine biochar quality and stability. Biochar type, biochar age, and soil type impact soil water relations and crop yields differently and therefore applications must be made strategically. More diverse crop rotations and biochar amendments enhance the long-term sustainability of Midwestern soils. Further, biochar C does not have the same effect on soil water parameters as biogenic OM, and the APSIM biochar model accurately predicts biochars impact on soil water and physical parameters when quality modifiers are used and local calibrations are made. Lastly, biochar applications are economically viable when coupled with other management practices in the Midwest, and can contribute to the long-term sustainability of agro-ecosystems.

References

Archontoulis, S.V., Huber, I., Miguez, F.E., Thorburn, P.J., Laird, D.A., 2016. A model for mechanistic and system assessments of biochar effects on soils and crops and trade-offs. GCB Bioenergy 8, 1028-1045. doi:10.1111/gcbb.12314

ASTM Standard D1762-84, 2007. Chemical Analysis of Wood Charcoal, ASTM International, West Conshohocken, PA, USA. http://dx.doi.org/10.1520/D1762-84R07

Bakshi, S., Aller, D., Laird, D., Chintala, R., 2016. Comparison of the physical and chemical properties of laboratory- and field-aged biochars, J. Environ. Qual. 45, 1627-1634. http://dx.doi.org/10.2134/jeq2016.02.0062

Gijsman, A., Jagtap, S., Jones, J., 2003. Wading through a swamp of complete confusion: how to choose a method for estimating soil water retention parameters for crop models. Eur J Agron. 18, 77-106.

Holzworth, D.P., Huth, N.I., deVoil, P.G., Zurcher, E.J., Herrmann, N.I., McLean, G., Chenu, K., van Oosterom, E.J., Snow, V.O., Murphy, C., Moore, A.D., Brown, H., Whish, J.P.M., Verrall, S., Fainges, J., Bell, L.W., Peake, A.S., Poulton, P.L., Hochman, Z., Thorburn, P.J., Gaydon, D.S., Dalgliesh, N., Rodriguez, D., Cox, H., Chapman, S., Doherty, A., Teixeira, E., Sharp, J., Cichota, R., Vogeler, I., Li, F.Y., Wang, E., Hammer, G.L., Robertson, M.J., Dimes, J.P., Whitbread, A.M., Hunt, J., van Rees, H., McClelland, T., Carberry, P.S., Hargreaves, J.N.G., MacLeod, N.D., McDonald, C.K., Harsdorf, J., Wedgwood, S., Keating, B.A., 2014. APSIM - evolution towards a new generation of agricultural systems simulation. Environ. Modell. Softw. 62, 327-350. doi.org/10.1016/j.envsoft.2014.07.009

Palmer, J., Thorburn, P.J., Biggs, J.S., Dominati, E.J., Probert, M.E., Meier, E.A., Huth, N.I., Dodd, M., Snow, V., Larsen, J.R., Parton, W.J., 2017. Nitrogen cycling from increased soil organic carbon contributes both positively and negatively to ecosystem services in wheat agro-ecosystems. Front. Plant Sci. 8, 731. doi: 10.3389/fpls.2017.00731

Saxton, K.E., Rawls, W.J., 2006. Soil water characteristic estimates by texture and organic matter for hydrologic solutions. Soil Sci. Soc. Am. J. 70, 1569-1578. doi:10.2136/sssaj2005.0117